Raman spectroscopy of layered metal chalcogenide 2D crystals

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**RAMAN SPECTROSCOPY OF LAYERED METAL
CHALCOGENIDE 2D CRYSTALS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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I thought that the acknowledgement section would be the easiest part to write of the whole thesis, just to find myself so wrong when I finally came to this very last part of my dissertation. Standing in front of the finishing line of my PhD journey and looking all the way back, all sorts of feelings are rushing into my head. Words just cannot express how grateful I feel right now about those people who helped me so much during the past long and short four years.

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Abstract

Two-dimensional (2D) atomic crystals represent a new class of materials, whose unusual physical and chemical properties arise due to their atomic thicknesses and low dimensionality. The van der Waals layered metal chalcogenide compounds, especially in their 2D forms, have drawn great attention during the past few years for their novel optical and electronic properties. In this report, we focus on the investigations on the physical properties related to lattice vibrations, *i.e.*, phonons, of two typical families of metal chalcogenides, the transition metal dichalcogenides (MoS_2 , MoSe_2 , WS_2 , WSe_2) and bismuth chalcogenides (Bi_2Se_3 , Bi_2Te_3), which are best known as the intriguing valleytronic materials and topological insulators, respectively. A comprehensive investigation on the phonon properties of these metal chalcogenide 2D crystals is conducted through a combination of Raman spectroscopy, group theory analysis, as well as first principles calculations.

High-quality 2D crystals have been successfully prepared for both transition metal and bismuth chalcogenides, through a mechanical exfoliation method and a vapor transport method, respectively. The 2D crystals exhibit excellent optical contrast on top of SiO_2/Si substrates, which enables the fast location and thickness determination of them simply through the optical microscopy. Moreover, a Te-seeded epitaxial growth mechanism has been uncovered for the vapor transport growth of Bi_2Te_3 nanoplates, which can be potentially extended to the growth of other metal chalcogenides through similar methods. Low-temperature electron transport measurements on the as-grown Bi_2Te_3 2D crystals reveals the weak anti-localization effect, as a result of the strong spin-orbit coupling in this topological insulator material.

The intrinsic phonon properties of the layered metal chalcogenides are largely affected by the crystal symmetry and dimensionality. Group theory analysis indicate that more phonon modes exist in 2D than 3D, and the phonon symmetries and optical activities are distinctively dependent on the layer number of the crystal. In general, while a Raman-active phonon mode in 3D should also be Raman-active in 2D, the reverse is not necessarily true. This crystal symmetry and dimensionality effect is best reflected in the characteristic

interlayer lattice vibrations of the layered materials. In both transition metal and bismuth chalcogenide 2D crystals, multiple interlayer breathing and shear modes have been uncovered through ultralow frequency ($<50 \text{ cm}^{-1}$) Raman spectroscopy, with perfect agreement with the first principles calculations. Some of these interlayer vibrational modes are absent in the 3D bulk limit, due to the higher crystal symmetry. The Raman observed interlayer shear modes show redshift and blueshift, respectively, in the transition metal dichalcogenide and bismuth chalcogenide 2D crystals with decreasing crystal thickness; while the interlayer breathing modes in both families exhibit blueshift. These frequency evolution trends versus crystal thicknesses can be quantitatively interpreted through a simple linear chain model.

The symmetry and dimensionality effect can also be reflected in the high frequency intralayer phonon property change from 3D to 2D. In the transition metal dichalcogenides, the intrinsic bulk phonon modes B_{2g}^1 and E_{1g} experience a Raman-forbidden to Raman-allowed symmetry transition from the 3D bulk to 2D crystals, and turn into Raman-forbidden symmetries again in the limit of monolayer. Moreover, the anomalous lattice vibrations, commonly known as the blueshift of the E_{2g}^1 mode and redshift of the A_{1g} mode with decreasing crystal thickness, have been identified through Raman spectroscopy in all the four transition metal dichalcogenide materials studied in this thesis. First principles calculations indicate the governing mechanism behind this phenomenon to be the competition between the surface effect and the thickness effect. Similarly, in bismuth chalcogenides, the Raman observed high frequency intralayer modes also exhibit frequency variations from 3D to 2D, as well captured by the calculated results. Besides the frequency changes, the Raman peaks generally experience broadening from 3D to 2D, which indicates a decrease of phonon lifetime and can be interpreted through the phonon confinement effect.

Overall, our results in this thesis reveal that crystal symmetry and dimensionality play the key role in determining the intrinsic phonon properties of the layered metal chalcogenides. This study sheds light on a general understanding of the phonon behaviors in all van der Waals layered materials and their evolutions from 3D to 2D.

Table of Contents

Acknowledgement	I
Abstract	III
Table of Contents.....	V
Citations to Published Work	VIII
Chapter 1 Introduction	1
1.1 Low-dimensional Nanomaterials	1
1.2 Layered Metal Chalcogenide 2D Crystals	4
1.2.1 Transition Metal Dichalcogenide 2D Crystals	5
1.2.2 Bismuth Chalcogenide 2D crystals.....	11
1.3 Lattice Vibrations in Layered Metal Chalcogenides.....	14
1.3.1 Lattice Vibrations-Phonons in Crystals.....	14
1.3.2 Group Theory Analysis of Phonon Modes	16
1.3.3 Phonon Properties in Layered Metal Chalcogenides	19
1.4 Motivation and Objectives of this Thesis	25
1.5 Organization of the Thesis.....	26
Chapter 2 Raman Spectroscopy.....	28
2.1 Basic Concepts of Raman Scattering	28
2.2 Theory of Raman Scattering.....	30
2.2.1 Classical Description	30
2.2.2 Quantum Description	32
2.3 Characteristics of Raman Spectra.....	35
2.3.1 Raman Spectral Lineshape and Linewidth	35
2.3.2 Stokes and Anti-Stokes Spectra.....	37
2.4 Raman Selection Rules	38
2.4.1 Energy and Momentum Conservation.....	38
2.4.2 Symmetry Selection Rule	39
2.5 Resonant Raman Scattering.....	42
2.6 Phonon Confinement Effect in Raman Spectroscopy.....	44
2.7 Instrumentation	47

2.7.1 Introduction to Horiba Jobin Yvon T64000 Spectrometer.....	47
2.7.2 Filtering of Laser Sidebands.....	50
Chapter 3 Sample Preparation and Characterizations.....	52
3.1 Mechanical Exfoliation of Transition Metal Dichalcogenide 2D Crystals.....	52
3.2 Synthesis and Characterizations of Bismuth Chalcogenide 2D Crystals.....	54
3.2.1 Vapor Transport Synthesis.....	55
3.2.2 Optical Contrast of Few-Quintuple Bi ₂ Te ₃ on SiO ₂ /Si Substrates.....	60
3.2.3 Te-Seeded Epitaxial Growth of Bi ₂ Te ₃ Nanoplates.....	63
3.2.4 Electron Transport Properties of Ultrathin Bi ₂ Te ₃ Nanoplates	71
Chapter 4 Ultralow Frequency Interlayer Breathing and Shear Modes in MX ₂ (M=Mo, W; X=S, Se) 2D crystals	81
4.1 Introduction.....	81
4.2 Raman Spectroscopy Measurements	82
4.2.1 Polarization Dependence.....	83
4.2.2 Thickness Dependence.....	86
4.2.3 Substrate Effect.....	91
4.3 Group Theory Analysis of Phonon Modes in MX ₂ 2D Crystals	93
4.3.1 Crystal Symmetries of Few-TL MX ₂	93
4.3.2 Irreducible Representations of Phonon Normal Modes.....	94
4.3.3 Interlayer Vibrational Modes in MX ₂ 2D Crystals.....	98
4.4 First Principles Calculations of Phonon Modes	99
4.4.1 Calculation Details.....	100
4.4.2 Phonon Normal Mode Assignment	101
4.4.3 Non-resonant Raman Intensity.....	108
4.5 Linear Chain Model.....	114
4.6 Summary.....	121
Chapter 5 High Frequency Intralayer Vibrational Modes in MX ₂ (M=Mo, W; X=S, Se) 2D Crystals.....	122
5.1 Introduction.....	122
5.2 Thickness Dependent Raman Measurements.....	123
5.3 Anomalous Lattice Vibrations in MX ₂ 2D Crystals.....	127
5.3.1 Frequency and Linewidth Evolutions from 3D to 2D.....	127
5.3.2 First Principles Calculations of Intralayer Phonon Modes.....	133

5.3.3 Surface Effect Versus Thickness Effect-A Physical Picture	140
5.4 Effect of Lower Dimensionality and Symmetry on Raman Spectra	146
5.4.1 Unexpected Raman Features in WSe ₂ 2D Crystals	146
5.4.2 Dimensionality Dependence of Phonon Symmetries	150
5.5 Summary.....	154
Chapter 6 Lattice Dynamics in Bi ₂ X ₃ (X=Se, Te) 2D Crystals	155
6.1 Introduction.....	155
6.2 Phonon Properties in 3D and 2D Bi ₂ X ₃	156
6.2.1 Irreducible Representations of Phonon Modes.....	156
6.2.2 Phonon Evolution Rule from 2D to 3D	158
6.3 Polarized Raman Spectroscopy	159
6.4 Ultralow Frequency Interlayer Vibrational Modes in Bi ₂ X ₃ 2D Crystals	161
6.4.1 Thickness-Dependent Raman Spectroscopy	161
6.4.2 First Principles Calculations.....	165
6.4.3 Linear Chain Model	169
6.4.3 Substrate Effect.....	172
6.5 High Frequency Intralayer Vibrational Modes in Bi ₂ X ₃ 2D Crystals.....	175
6.5.1 Frequency and Linewidth Evolutions	175
6.5.2 First Principles Calculations.....	180
6.6 Summary.....	184
Chapter 7 Conclusions and Future Work	185
7.1 Conclusions.....	185
7.2 Future Work.....	187
References	192
Publications	201

Citations to Published Work

Majority of Chapter 3 appears as:

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“Anomalous Frequency Trends in MoS_2 Thin Films Attributed to Surface Effects” X. Luo, Y. Zhao, J. Zhang, S. Y. Quek, and Q. Xiong. *Physical Review B* 88, 075320 (2013)

Chapter 1 Introduction

1.1 Low-dimensional Nanomaterials

“*Dimension*” is a widely used concept in a variety of subjects, from mathematics, physics to philosophy and literature. The dimension of a space or physical object refers to the minimum number of coordinates needed to specify a point within it, according to which the world we are living in is defined to be three-dimensional. Physicists and mathematicians are never satisfied with this limitation of our three dimensions and they thus theoretically create all sorts of abstract higher dimensional worlds that are beyond our imagination. Worlds of different dimensions are completely different while closely related, as vividly presented in the popular science series “*Flatland: A Romance of Many Dimensions*”, and two sequels “*Sphereland*” and “*Flatterland*”,^{1, 2} where “a square” from a two-dimensional space gets to experience the wonders in different dimensions. We do not have the luxury to wander around in higher-dimensional spaces as the “square” does, while we are fortunately granted the possibility to peek into the worlds of lower dimensions by studying low-dimensional objects-nanomaterials.

The prefix “*nano*” origins from the ancient Greek word “*nanos*” meaning dwarf, and denotes a billionth (10^{-9}) in the metric system. Nanomaterials refer to materials with a size of 1 to 100 nanometers (nm) in at least one dimension. Structures with three, two and one dimensions within nanoscale are named zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) nanostructures (strictly speaking, these are quasi-0D, 1D and 2D), respectively. The best examples of 0D, 1D and 2D nanostructures are quantum dots,³ quantum wires,⁴ quantum wells and heterostructures⁵ in the semiconductor systems, and fullerenes,⁶ carbon nanotubes,⁷ and graphene⁸ in the carbon material system. Physics becomes interesting in the low-dimensional nanoscale regime, where the classical Newton’s laws become vulnerable and quantum mechanics pop in.⁹ One good example is the electron transport properties of solids. The scaling theory predicts that metal-insulator transition only exists in three dimensions, while in one and two dimensions, the insulating regime is eventually reached in the thermodynamic limit at zero temperature.¹⁰ Ballistic conduction has been observed in quantum wires and carbon nanotubes,^{11, 12} due to the

quantization of conductance in the 1D regime. Moreover, the “exact quantization” of conductance-integer quantum Hall effect, has been demonstrated in the 2D electron systems-gallium arsenide heterostructures in early 1980’s and also recently in graphene.¹³
¹⁴ In the same systems, fractional quantum Hall effect was also identified as a unique collective behavior of the 2D electrons, which represents a new quantum fluid and its fractionally charged quasiparticles.¹⁵⁻¹⁷ The discovery and understanding of the integer and fractional quantum Hall effects set important milestones in the history of condensed matter physics, and were rewarded the Nobel Prize in physics in 1985 and 1998, respectively. The list of new physical phenomena in nanomaterials can go on and on with numerous examples. Overall, the vigorous development of nanoscience and nanotechnology for the past three decades has demonstrated the low-dimensional nanomaterials as excellent platforms for fundamental research as well as new opportunities for potential applications, attributed to their unique physical and chemical properties.

One important fundamental difference between different dimensions is the electron behavior, which is closely related to the optical and electrical properties of the material. When the movement of electrons is spatially confined into certain directions, both the electronic structure and density of states (DOS) will be largely modulated. Consider a simple model where free electrons are put into a three-dimensional box with volume of $\Omega = L_x \times L_y \times L_z$,⁹ with the periodic boundary conditions, the energy dispersion of this system in the momentum space can be represented by

$$E(k_x, k_y, k_z) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 K^2}{2m}, \quad (1-1)$$

where m is the mass of electron and $K = (\frac{2\pi l}{L_x}, \frac{2\pi m}{L_y}, \frac{2\pi n}{L_z})$ with $l, m, n = 0, \pm 1, \pm 2, \dots$

These states are evenly distributed in the K -space along each direction k_x, k_y or k_z . When the box is infinitely large, all the quantized states will become continuous and the DOS as a function of energy can be described by $n_{3D}(E) = \frac{m}{\pi^2 \hbar^3} \sqrt{2mE}$, as shown by Figure 1-1a.

Similarly, in the case of a 2D box, where $L_x, L_y \rightarrow \infty$ while L_z is finite, the available states

will be continuous in k_x and k_y directions while remain quantized along the k_z direction. Consequently, the DOS in 2D will become irrelevant to the energy (E^0 dependence) and form a plateau shape, as shown in Figure 1-1b. Further decreasing the dimension of the box to 1D, the eigenstates will be continuous along only one axis in the momentum space.

Thus, the DOS would show a $\frac{1}{\sqrt{E}}$ energy dependence, and displays as a spike for each quantized state known as the von Hove singularity, as shown as Figure 1-1c. Furthermore, in the limit of 0D, all the energy states remain quantized along all axes of the K -space and the DOS show as discrete lines (Figure 1-1d). Note that the Figure 1-1 represents the quasi-2D, 1D and 0D situations, where the multiple steps, spike and lines shown in the density of states will reduce to a single one in the absolute 2D, 1D and 0D cases.

Figure 1-1 Density of states of a free electron in 3D, as well as when confined in quasi-2D (b), quasi-1D (c), and quasi-0D (d) conditions.¹⁸

Dimensionality dependence of the electron density of states is a good example of the quantum confinement effect, which takes place when the size of the material is small enough and becomes comparable to the magnitude of the electron wavelength.^{19, 20} Quantum confinement effect can substantially deviate the optical and electronic properties of the low-dimensional materials from those of their bulk counterparts and is very common in semiconductor nanostructures. In the 2D quantum well system where a thin layer of GaAs is sandwiched by two thick layers of AlGaAs, discrete excitonic states can form due to the special confinement. Electron transitions between these discrete excitonic states can be reflected by the optical absorption and photoluminescence spectroscopy.⁵ Similar

confined discrete states in 0D have been identified through electronic transport measurements in GaAs quantum dots,²¹ and through optical absorption in CdSe quantum dots.²² Besides, the photoemission energy of quantum dots can be largely tuned through the size and shape control, which again, is a result of the quantum confinement effect when the quantum dot is smaller than the Bohr radii of the excitons in the bulk.^{23, 24} The unique optical properties of quantum dots lead to the promising applications in light-emitting diodes, solar cells, and diode lasers, *etc.* Quantum confinement could also be responsible for the diameter dependence of the electronic structures,²⁵ photoluminescence,²⁶ photoconductivity,²⁷ and phonon properties²⁸ in ultrathin semiconductor nanowires.

In summary, the low-dimensional nanostructures are a golden field for the condensed matter physics research due to the prominent quantum confinement effect. More and more novel physics are expected to emerge from these low-dimensional systems.

1.2 Layered Metal Chalcogenide 2D Crystals

2D crystals with atomic thicknesses represent a perfect playground for investigating the physics in low dimensions. 2D crystals were speculated to be thermodynamically unstable because the thermal fluctuation becomes so strong that the displacement of 2D lattice is comparable to the lattice constant at finite temperature.²⁹⁻³¹ This speculation was overturned by Novoselov and Geim in 2004 through the isolation of atomic thin graphene layers from graphite.³² Since then, graphene has become one of the most fast growing research areas in physics. With a single layer of carbon atoms in the honeycomb lattice, graphene possesses a unique electronic structure, which gives rise to a lot of exotic physical phenomena and enables the study of “Fermi-Dirac” physics in condensed matter. In the past decade this “super-material” has demonstrated its versatility for fundamental and technological research in a wide range of areas including transparent electric and thermal conductors,^{33, 34} high-speed electronic and optoelectronic devices,^{35, 36} energy generation and storage,³⁷ catalysis,³⁸ chemical/bio sensing,³⁹ DNA sequencing,^{40, 41} *etc.* In 2010, Novoselov and Geim were rewarded the Nobel Prize in physics “*for groundbreaking experiments regarding the two-dimensional material graphene*”.

The great success of graphene research also lead people's attention to other 2D crystals beyond graphene for more opportunities. Just as graphene can be isolated from graphite, 2D atomic crystals in general could be isolated from their corresponding bulk layered materials, some of which are traditionally well-known as dry lubricants.⁴² There exists a large variety of layered materials in nature, ranging from insulators such as BN, semiconductor such as MoS₂, semimetals like TiSe₂, to true metals like VSe₂, and even superconductors like NbSe₂. Except for a couple of elementary substances like graphite and black phosphorous, most of the layered materials are transition metal chalcogenide compounds, and only a few are IIIA, IVA, VA metal chalcogenides like GaS, SnS₂, and Bi₂Te₃.^{42, 43} These layered materials are often referred to as van der Waals (vdW) materials since they can be considered as stacking of 2D monolayers bonded through vdW interactions. A monolayer unit could represent a single atomic layer (like graphene), or several atomic layers that are covalently bonded (like MoS₂). Because of the weak vdW interactions between the unit layers, single or few monolayers could be easily isolated from the bulk crystal, using some top-down methods like mechanical or chemical exfoliation.^{44, 45} 2D crystals can also be synthesized through bottom-up methods, such as molecular beam epitaxy,^{46, 47} chemical vapor deposition,^{48, 49} wet chemistry synthesis,⁴⁷ *etc.* All the above methods have their own limitations and the choice of method depends on the material as well as the focus of research.

1.2.1 Transition Metal Dichalcogenide 2D Crystals

The transition metal chalcogenide family includes more than 40 layered compounds with a stoichiometry of MX₂, where M represents transition metal (Ti, Hf, Mo, W, Rc, Pd, *etc.*) and X stands for the chalcogen atoms (S, Se, Te).^{42, 50} So far, the most extensively studied transition metal dichalcogenides (TMD) are Mo and W chalcogenide 2D crystals for their novel optical and electronic properties.

MX₂ (M=Mo, W; X=S, Se) share the same hexagonal crystalline structure, as shown in Figure 1-2. Each layer is composed of three atomic layers, one M layer sandwiched between two X layers, and we therefore refer them as a trilayer (TL) with a thickness of around 0.7 nm. The M and X atoms could occupy different trigonal sites, forming different

polytypes. For Mo and W dichalcogenides, 2H (here H stands for hexagonal) is the most stable and common polytype in nature, where two adjacent atomic layers keep alternating at A and B sites, as shown in Figure 1-2a. The two different atomic sites can be better displayed from the top view of a single TL MX₂ (Figure 1-2b).

Figure 1-2 Crystal structure of 2H-MX₂ from (a) side view (b) and top view. The hexagonal planes of M and X atoms follow /AB/ stacking.

With the same crystalline structure, MX₂ have very similar electronic characteristics. The most exotic property of MX₂ is its thickness-dependent electronic structure, where an indirect-to-direct band gap transition takes place from bulk crystals to the limit of single TLs. This electronic characteristics can be depicted by the theoretical calculations. Figure 1-3a shows the first principles calculated band structures of bulk, 4TL, 2TL, and 1TL MoS₂ without considering the spin-orbit coupling.⁵¹ In the bulk, the indirect band gap is around 1.3 eV with the valence band maximum at Γ point and the conduction band minimum somewhere between the Γ and K points, as denoted by the black arrow. With decreasing thickness, the indirect band gap keeps enlarging and becomes larger than the direct band gap at the K point in the case of 1TL. This indirect-to-direct band gap transition was first experimentally confirmed by Mak *et al.* through the photoluminescence and photoconductivity studies on mono- and few-TL MoS₂, where the photoluminescence quantum yield of 1TL MoS₂ has been found to be 2 orders higher than 2TL, and 4 orders higher than the bulk.⁵² They also found that the photoluminescence quantum yield for 1TL MoS₂ can be further enhanced by suspending the sample. Similar thickness-dependent band structure change has also been confirmed by theoretical calculations as well as photoluminescence spectroscopy in MoSe₂, WS₂ and WSe₂ 2D crystals.⁵³⁻⁵⁷ The electronic

structures of MX_2 2D crystals can be largely affected by strain and external electric field. First principles calculations indicate that strain allows engineering the magnitude of the band gap as well as the indirect or direct characteristics, which were experimentally verified.⁵⁸⁻⁶⁰ Furthermore, the band gaps of MX_2 2D crystals can be effectively tuned by transverse and perpendicular fields from semiconductor to metal regime, with symmetry-related thickness dependence.⁶⁰⁻⁶²

Figure 1-3 (a) First principles calculated band structure of bulk and few-TL MoS_2 , indicating an indirect-to-direct band gap transition at 1TL.⁵¹ (b) Calculated electronic structure of 1TL MoSe_2 with consideration of spin-orbit coupling. The energy difference between A and B excitons is around 180 meV.⁶³ (c) Normalized photoluminescence spectra of 1-6TL MoS_2 . The direct-gap A and B excitons and indirect-gap transitions (I) are identified.⁵² (d) 2D mapping of photoluminescence intensity versus back gate voltage in a 1TL MoSe_2 field effect transistor (FET) device. X^0 , X^+ , X^- , and X^I refer to the neutral (A), positively charged, negatively charged, and impurity induced excitons, respectively. The schematic on the right illustrates the gate-dependent trion and exciton quasi-particles and transitions.⁶³

Besides the indirect-to-direct band gap transition, the strong spin-orbit coupling of MX_2 originating from the d orbitals of the transition metal Mo and W leads to more interesting

excitonic properties. Considering the spin-orbit coupling, the band-edge states at the K point will split into two branches. Figure 1-3b shows the first principles calculated band structure of 1TL MoSe₂, where there is a splitting of 180 meV at the valence band top at the K point, while the splitting of the conduction band bottom is negligible. The magnitude of valence band top splitting varies in different materials and has been estimated to be around 130 meV, 430 meV, 470 meV in 1TL MoS₂, WS₂, and WSe₂, respectively.^{52, 55} Band-edge optical transitions at the K point are referred to as A and B excitons (Figure 1-3b), which can be experimentally characterized through absorption and photoluminescence spectroscopy. Figure 1-3c displays the normalized photoluminescence spectra of 1-6TL MoS₂, where the A and B excitons at the K point and the indirect gap transition (I) can be identified. A and B excitons have been theoretically predicted to be strongly bonded excitons with large binding energies of up to 1 eV in monolayer Mo and W dichalcogenides,⁶⁴ while later this value was identified to be 0.32 eV for 1TL WS₂ through optical reflection measurements,⁶⁵ and be 0.57 eV for 1TL MoS₂ through photocurrent spectroscopy.⁶⁶ Besides the neutral excitons, charged excitons (also known as trions), a quasiparticle composed of an exciton and an electron/hole can also be optically created and detected, and the density of the trions can be dynamically controlled by doping in a FET device (Figure 1-3d).^{63, 67} Most recently, the exciton dynamics in MX₂ 2D crystal heterostructures, where effective charge transfer and interlayer excitons have been identified.⁶⁸

Recently, MX₂ 2D crystals are found to offer great opportunities to a new generation of electronic devices which rely on the valley degree of freedom of the electrons-valleytronics. Valley polarization, the core of valleytronics, has been demonstrated in graphene and 2D electron gas systems using strain and magnetic field.⁶⁹⁻⁷¹ While in monolayer MX₂, coupled spin and valley polarization can be naturally achieved, due to inversion symmetry breaking and strong spin-orbit coupling.⁷² Figure 1-4a shows the band structure of monolayer MX₂ at the band edges at the K points. The two split valence band tops at a given valley corresponding to A and B excitons are spin-polarized. Moreover, the spin-polarization is reversed for K and K' (-K) valleys, leading to a valley- and spin-dependent optical selection rule. If illuminating the MX₂ monolayers by a circularly polarized light, only K (or K') valleys can be populated by electrons, and the optical

selection rule remains for the photoemission process, resulting in an emitted light with the sample polarization as the incident one. Selective valley population has been experimentally demonstrated through helical optical pumping by several groups.⁷³⁻⁷⁸ The degree of optical polarization is defined as $\rho = \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}}$, where I_{σ^+} and I_{σ^-} are emitted light with right and left circularly polarized light, respectively. A polarization of up to 100% has been achieved by Mak *et al.* in monolayer MoS₂ with an on resonance pumping at low temperature, shown at Figure 1-4b.⁷³ The helical polarization holds for both neutral and charged excitons. Furthermore, excitonic valley coherence has been explored by Jones *et al.*,⁷⁸ where they found that two coherent valley states (K and K') can be generated through a linearly polarized light, resulting in the linear polarization of the neutral exciton in monolayer WSe₂, as shown in Figure 1-4c. Recent research shows that spin and valley physics in MX₂ 2D crystals could lead to a lot more novel phenomena, such as the valley Hall effect,^{72,79} spin-layer locking effect,⁸⁰ and the coherent coupling between excitons and trions,⁸¹ *etc.*

Figure 1-4 (a) Schematic of the spin-polarized band-edge states of monolayer MX₂.⁷² (b) σ^+ and σ^- resolved photoluminescence spectra of monolayer MoS₂ with on resonance excitation (left panel) and corresponding degree of optical polarization (right panel).⁷³ (c) Linear polarization resolved photoluminescence spectra of monolayer WSe₂ with parallel (black curves) and perpendicular (red curves) polarization configurations.⁷⁸ The neutral exciton exhibits linear polarization while the charged excitons do not.

Aside from their interesting optical properties that are closely related to the intriguing electronic structures, MX_2 2D crystals also attracted intense interest for the electronic device investigations, such as FETs, photodetectors, photodiode, *etc.* Monolayer MoS_2 transistors were theoretically predicted by Salahuddin *et al.* to be ideal for low power applications attributed to their large on-off current ratio, immunity to short channel effect, and fast switching.⁸² A large amount of experimental works have been devoted to investigate the performance of MoX_2 2D crystal transistors, and ambipolar transport has been achieved in many cases with high on-off ratio up to 10^8 .^{44, 83-87} In most back-gated FET devices on SiO_2/Si substrates, the charge carrier mobility is generally within the range of $0.1\text{-}50\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, much lower than that of Si.⁸⁶ The carrier mobility was later found to be dependent on substrates due to the dielectric screening effect and can be largely enhanced by using other substrates like Al_2O_3 and PMMA,^{88, 89} or by adopting a dual-gated geometry with a high- k dielectric top layer.^{83, 90} High-performance MX_2 2D crystal FET devices can serve as building blocks for logic gates and integrated circuits. This has been recently demonstrated by Kis *et al.* and Palacios *et al.* on monolayer and bilayer MoS_2 , respectively, where several different integrated circuits have been successfully fabricated with logic operations, such as a logic inverter, a NAND gate, a static access memory cell, and a five-stage ring oscillator.^{87, 91} The tunable band gaps of MX_2 2D crystals through thickness, strain, and chemical functioning make them attractive as light-absorbing materials and optoelectronic applications.⁹⁰ Monolayer MoS_2 phototransistors with metal-semiconductor contacts show high photoresponse in the visible range with a maximum external photoresponsivity of up to 880AW^{-1} .⁹² The photodetector performance can be largely enhanced in a $\text{MoS}_2/\text{graphene}$ heterostructure, where the photo-generated electron-hole pairs can be effectively separated and transfer to graphene, instead of being trapped in the MoS_2 layer.⁹³ The graphene/ MX_2 /graphene heterostructures are further taken advantage of as highly efficient photocurrent generators and photodiodes.^{94, 95}

Bulk transition metal dichalcogenide compounds have been known and studied for decades, while the research of their 2D form is still a nascent field. TMD 2D crystals open a door to new scientific frontiers such as the spin-valley physics, which is expected to lead to a new generation of technology-valleytronics. The intriguing transition of their electronic and optical characteristics from 3D to the 2D limit reveals the importance of

dimensionality. TMD 2D crystals provide an excellent platform with rich physics in two dimensions, the understanding of which will potentially lead to unanticipated fundamental phenomena and their practical applications.

1.2.2 Bismuth Chalcogenide 2D crystals

Bulk bismuth chalcogenide (Bi_2Se_3 and Bi_2Te_3) crystals have a layered structure with rhombohedral crystalline symmetry,^{96, 97} as shown in Figure 1-5a. Each layer in Bi_2X_3 ($\text{X}=\text{Se}, \text{Te}$) is composed of five trigonally packed atomic layers with a sequence of $\text{X}_1\text{-Bi-X}_2\text{-Bi-X}_1$ and thus is referred to as a quintuple layer (QL), whose thickness is around 1 nm. The subscripts 1 and 2 denote two inequivalent positions for the X atoms. Two QLs are bonded interacting through a weak vdW force while the atoms are strongly bonded through covalent interactions within one QL. There are in total three different types of atomic sites for all the Bi and X layers, which are stacked along the out-of-plane c axis following the /ABC/ order. Therefore, the primitive unit cell of the bulk Bi_2X_3 overruns three QLs and contains five atoms, as shown by the black polyhedron in Figure 1-5a.

Figure 1-5 (a) Crystalline structure of $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Se}_3$. The primitive unit cell is indicated by the polyhedron (black solid lines). The lattice vectors of the unit cell are shown as the arrows denoted by b_1, b_2, b_3 . (b) Schematic of the band structure of the topological insulators. The surface states have a linear dispersion at the vicinity of the Brillouin zone

center and are spin-polarized.⁹⁸ (c) ARPES measurements of surface electronic band dispersion on bulk crystal Bi₂Se₃.⁹⁹

Bismuth chalcogenides are excellent thermoelectric materials and are commonly used in the thermoelectric industry. The performance of a thermoelectric device is characterized by its dimensionless figure of merit given by $ZT = \frac{\sigma S^2 T}{\kappa}$, where S is the Seebeck coefficient, T is temperature, σ and κ are the electrical and thermal conductivities of the material, respectively.¹⁰⁰ Due to their high Seebeck coefficient, low thermal conductivity and high electrical conductivity, bismuth chalcogenide based ternary and quaternary compounds and alloys in the bulk form represent the state-of-art thermoelectric devices which can achieve a figure of merit of above 1 at room temperature and even to 2 at high pressure.^{100, 101}

After being known for their thermoelectric properties for decades, Bi₂Te₃ and Bi₂Se₃, together with Sb₂Te₃, were theoretically predicted in 2009 to be three-dimensional topological insulators, a new state of quantum matter which has gaped bulk states but conducting surface states, shown as Figure 1-5b.¹⁰² The surface states with the shape of a Dirac cone locates at the center of the Brillouin zone, fulfilling the bulk band gap, which is around 0.1 eV for Bi₂Te₃ and 0.3 eV for Bi₂Se₃. Due to the strong spin-orbit coupling of these materials, as well as the time reversal symmetry, the surface states are spin-polarized and robust against any non-magnetic impurities and scatterings. The topological surface states have been experimentally confirmed through angular resolved photoemission spectroscopy (ARPES) in bulk Bi₂Se₃ and Bi₂Te₃ crystals, as shown in Figure 1-5c.⁹⁹ The intriguing surface states make topological insulators an attractive platform for fundamental research as well as potential applications in spintronics, quantum computing, and low-energy dissipation electronics.^{98, 103, 104}

Bismuth chalcogenides in 2D form are advantageous to their bulk counterparts, for both thermoelectric and topological insulating properties. The thermoelectric performance can be largely enhanced in two dimensions thanks to a higher Seebeck coefficient (S) resulted from an increased density of states, as well as a reduced thermal conductivity (k) due to a stronger phonon scattering by the surface.¹⁰⁵ Venkatasubramanian *et al.* achieved a ZT up

to 2.4 at room temperature on a $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ thin-film superlattice due to the phonon-blocking/electron-transmitting effect.¹⁰⁶ Enhanced thermoelectric properties have also been demonstrated in a device composed of well-aligned and compacted bismuth chalcogenide nanoplates due to the poor thermal conductivity and charge carrier filtering through grain boundaries and interfaces.^{107, 108} Bi_2X_3 2D crystals are also preferable for the studies of the topological insulating properties because of (1) the enhanced surface state contribution due to the extremely large surface-to-volume ratio; and (2) the enlarged bulk band gap caused by quantum size effect, which allows wider operation ranges for spintronic devices. Recent transport measurements have reported the ambipolar field effect, Aharonov-Bohm (AB) effect and Shubnikov-de Haas (SdH) oscillations in topological insulator thin films that are associated with the surface states.¹⁰⁹⁻¹¹² Unusual physical phenomena might occur in the 2D limit. ARPES measurements demonstrated that a gap will open up at the Dirac point of the topological surface states below 6 QLs for Bi_2Se_3 and 4 QLs for Bi_2Te_3 , turning from nontrivial topological insulators to trivial insulators.^{113, 114} Most recently, the theoretically predicted quantum anomalous Hall effect has been experimentally achieved in magnetically doped topological insulator thin films, which is an important breakthrough for the research of topological insulators.¹¹⁵

Besides their well-known thermoelectric and topological insulating properties, bismuth chalcogenide thin films have also been theoretically proposed for high-performance photodetection covering a broad spectrum range from terahertz to infrared (IR) due to their intrinsic bulk band gaps and the gapless surface states.¹¹⁶ Moreover, in analogy to graphene, thin layers of bismuth chalcogenides could have huge potential in optoelectronic applications such as terahertz lasers, plasmon-based radiation generation and detection, and near-IR transparent electrodes, *etc.*,¹¹⁶ the latter of which has been successfully demonstrated by Peng *et al.* on few-QL Bi_2Se_3 on mica substrates through chemical vapor deposition.⁴⁹

1.3 Lattice Vibrations in Layered Metal Chalcogenides

1.3.1 Lattice Vibrations-Phonons in Crystals

In a crystal, the atoms or ions at the lattice sites are never still, instead, they keep deviating from their equilibrium positions in a collective manner. The energy cost for the atom motions in crystals is quantized, and therefore the lattice vibrations can be treated as quasiparticles with single frequencies, also known as phonons.¹¹⁷

The frequency of a phonon mode in a crystal can be obtained by solving the classical equation of motion for the ions

$$M_i \ddot{u}^i = \sum_j K^{ij} (u^j - u^i), \quad (1-2)$$

where M_i is the mass of the ion at an arbitrary lattice site i , and $u^i = (x_i, y_i, z_i)$ defines its deviation from its equilibrium position under the Cartesian coordinates.¹¹⁷ K^{ij} is the force constant induced by the relative locations between the ions at site i and j and here represents a 3×3 tensor. K^{ij} is usually taken over several neighbor distances, considering the long-range Coulomb interactions between ions. When the long-range interaction is very weak, or for a qualitative investigation, one can assume that K^{ij} vanishes unless the sites i and j are the nearest neighbors. In a periodic lattice, according to Bloch's theorem, a solution can be posted to equation (1-2) with the form of

$$u^i = \varepsilon \cdot e^{i(k \cdot R_i - \omega t)}, \quad (1-3)$$

where the lattice vibration can be treated as a propagating wave with frequency ω and wave vector k . ε is the unit vector describing the polarization of the vibration and R_i characterizes the i^{th} lattice site. Solving equation (1-2) and (1-3) over all the N atoms within a unit cell, one can get the phonon dispersion relations $\omega(k)$ for all the vibrational normal modes across the Brillouin zone. The analytical solution to equation (1-2) can be well presented in a simple 1D chain with two different atoms M_1 and M_2 with a lattice period a ,

as shown in Figure 1-6a. Taking the nearest neighbor approximation, equation (1-2) becomes

$$\begin{aligned} M_1 \ddot{u}_1^i &= K(u_2^i - 2u_1^i + u_2^{i-1}) \\ M_2 \ddot{u}_2^i &= K(u_1^{i+1} - 2u_2^i + u_1^i) \end{aligned} \quad (1-4)$$

Here, K^{ij} becomes a constant K . Substituting equation (1-3) to equation (1-4), we get

$$\omega = \sqrt{K} \sqrt{\frac{M_1 + M_2 \pm \sqrt{M_1^2 + 2M_1M_2 \cos ka + M_2^2}}{M_1M_2}}. \quad (1-5)$$

The two branches of phonon dispersions are displayed in Figure 1-6b. The frequency of one branch goes to zero when $k \rightarrow 0$, and has a linear dispersion near the zero momentum. Phonons in this branch are called acoustic modes since they behave like an ordinary sound wave. The other branch has a finite frequency at zero momentum and is referred to as the optical branch since they can often be excited by photons. The vibrations of the zero-momentum acoustic and optical phonons in the 1D chain are depicted in Figure 1-6a, where all the atoms in the unit cell are vibrating in phase for the acoustic mode, corresponding to its zero frequency; while out-of-phase vibrations exist in the unit cell for the optical mode. The wave vector k of a phonon mode characterizes a phase change of a unit cell respecting to neighboring unit cells; while for the Γ point phonons ($k=0$), the phase change is zero and all the unit cells are displacing identically.¹¹⁸ The largest possible wave vector of a phonon mode is at the Brillouin zone boundary $\pm \frac{\pi}{a}$ and any values larger than that can be folded back to the first Brillouin zone. The polarization direction ε (direction of the vibration amplitude) of a phonon mode could be parallel or perpendicular to its wave vector k , corresponding to longitudinal and transverse waves, respectively.

Figure 1-6 (a) Schematic of the 1D diatom chain, and the zone center acoustic and optical phonons. (b) Schematic phonon dispersion of the 1D chain, displaying the acoustic and optical phonon branches.

In a three-dimensional crystal with N atoms within a primitive unit cell, there are $3N$ degrees of freedom and thus $3N$ branches of phonon normal modes, among which 3 are acoustic branches and the rest are optical branches. Based on the phonon polarization, these $3N$ branches could be further specified as longitudinal acoustic (LA), transverse acoustic (TA), longitudinal optical (LO) and transverse optical (TO) branches. Since most crystals are anisotropic, the phonon dispersions vary along different directions (k) in the reciprocal space. The 3D mapping of phonon dispersion is complicated and phonon dispersions along certain high symmetry point are generally considered. The phonon dispersion relation captures all the information on the lattice vibrations in a crystal and is essentially important for interpreting the experimental data on neutron scattering, IR absorption, Raman and Brillouin spectroscopy, *etc.*

1.3.2 Group Theory Analysis of Phonon Modes

Symmetry is a very important concept in Physics and it governs a lot of selection rules for electronic and optical transitions. The lattice vibrations of a crystal, in terms of allowed vibrational normal modes and their optical activities, are dictated by the symmetry of the crystal lattice. Group theory provides a powerful mathematical tool to analyze the phonon properties from the crystal symmetry, by transforming many complex symmetry operations into simple linear algebra.

The definition of a group in the group theory has a very broad sense as long as the group elements meet certain multiplication rules. In crystallography, the group elements are a set of symmetry operations that a crystal exhibits, such as inversion (i), rotation (C), reflection (σ), ..., *etc.* These symmetry operations need to be presented in the form of square matrices, which is known as the representation of the group element. The representation of a symmetry operation R in group Γ is defined by $D(R)$ as

$$Ru = D(R)u, \quad (1-6)$$

where $D(R)$ is a second-rank m -dimensional tensor and $u = (u_1, u_2, \dots, u_m)$ is a set of basis functions that $D(R)$ operates on.¹¹⁹ Generally, the representations of all the elements in the group can be blocked into sub-matrices by one unitary transformation $UD(R)U^{-1}$ into the form

$$UD(R)U^{-1} = \begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{pmatrix}, \quad (1-7)$$

where D_1, D_2, D_3 are square matrices with dimensions smaller than m . $D(R)$ is called a reducible representation in this case, and the basis functions are also decomposed into smaller dimensions. D_1, D_2, D_3 here are called irreducible representations. Note that the sub-matrices D_1, D_2, D_3 for each group element representation can form new groups $\Gamma_1, \Gamma_2, \Gamma_3$ that are either isomorphic or homomorphic to the group Γ , that is to say, $\Gamma_1, \Gamma_2, \Gamma_3$ obey the multiplication rules of Γ . Any reducible representation of a group can be listed as the sum of all the irreducible representations:

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3. \quad (1-8)$$

The irreducible representation of a matrix is very important since the lower dimensions of the matrix blocks make the algebra much easier to manipulate than the original reducible symmetry operations.

For the phonon analysis through group theory, one needs to well understand all the symmetry operations in the crystal. In crystallography, there exist 32 point groups in three

dimensions where all the basic symmetry operations are conducted with respect to a specific point. The symmetry of a 3D crystal can be characterized by point groups with translation symmetry, also known as space groups with 230 types in total. All the information of the Brillouin zone center phonons ($k=0$) can be captured by the point group that the crystal belongs to, while the description of phonon modes with finite momentum ($k \neq 0$) needs to involve the space groups since the translation symmetry becomes important. Here, we will focus on the group theory analysis of zone center phonons since the $k \neq 0$ phonons are generally not very important in Raman spectroscopy.

The first step to find the vibrational normal mode of a crystal is to analyze all the possible symmetry operations and identify its point group symmetry. This step could be tedious and complex. Fortunately, all the 32 point groups have been well studied by previous mathematicians and physicists and all the information on the specific point group can be found in its character table, including its the related symmetry operations, irreducible representations and basis functions. The common basis functions given in a point group character table include the linear translation functions x , y , z , the rotation functions R_x , R_y , R_z , and the quadratic functions xx , yy , zz , xy , yz , zx , *etc.* After knowing the point group of the whole crystal, the next step is to identify the symmetry operations on each atomic site and get the representation $\Gamma_{atom \ sites}$, which is normally a reducible representation of the crystal point group and needs to be decomposed into its irreducible representations following equation (1-8). The lattice vibration of a crystal involves the transformation properties of a vector, which in group theory means that the phonon modes can be found by the direct product of $\Gamma_{atom \ sites}$ and the irreducible representations of a radial vector Γ_{vec} :

$$\Gamma_{phonon} = \Gamma_{atom \ sites} \otimes \Gamma_{vec} . \quad (1-9)$$

Γ_{vec} can be obtained by summing the irreducible representations to which the basis functions x , y , z belong.¹¹⁹ Equation (1-9) can be calculated according to the product table of the point group of the crystal that can be found in many group theory textbooks.¹²⁰

Now we use the monolayer MoS₂ as an example to demonstrate the group theory analysis of the phonon modes at the Brillouin zone center. Monolayer MoS₂ belongs to

point group D_{3h} which includes the following symmetry operations E , $2C_3$, $3C_2'$, σ_h , $2S_3$, $3\sigma_v$. By analyzing the above sequence of symmetry operations on both Mo and S sites, we found that the invariant atom sites are 3, 3, 1, 1, 1, 3, respectively. Note that invariant number of atoms are equivalent to the characters of the irreducible representations of the point group D_{3h} , we therefore can decompose $\Gamma_{atom\ sites}$ into the below irreducible representation

$$\Gamma_{atom\ sites} = 2A_1' + A_2'' . \quad (1-10)$$

Through the character table of the point group D_{3h} , we can find that $\Gamma_{vec} = E' + A_2''$. The irreducible representation of the phonon modes in monolayer MoS₂ can be obtained as

$$\begin{aligned} \Gamma_{phonon} &= (2A_1' + A_2'') \otimes (E' + A_2'') \\ &= 2E' + E'' + 2A_2'' + A_1' . \end{aligned} \quad (1-11)$$

The Raman and IR activity of a phonon mode can also be reflected from the character table of the point group. If a phonon mode happens to have the same irreducible representation as the linear basis functions, this phonon is IR-active; if a phonon has the same irreducible representation as the quadratic basis functions, it is Raman-active.¹¹⁹ A phonon mode could be both Raman-active and IR-active, or neither, which is known as a silent or optically inactive phonon mode.

1.3.3 Phonon Properties in Layered Metal Chalcogenides

The phonon properties can be analyzed according to the group theory, as discussed in the previous section. Bulk 2H-MX₂ (M=Mo, W; X=S, Se) belong to the space group D_{6h}^4 ($P6_3/mmc$). The primitive unit cell overruns two TLs (six atoms), and therefore there exists 18 Brillouin Zone center (Γ) phonons. The irreducible representations of the Γ phonon modes can be written as $\Gamma_{bulk} = A_{1g} + 2A_{2u} + B_{1u} + 2B_{2g} + E_{1g} + 2E_{1u} + E_{2u} + 2E_{2g}$, where the three acoustic phonon modes have A_{2u} and E_{1u} symmetries, respectively. There

exist four Raman-active optical modes ($2E_{2g}$, E_{1g} and A_{1g}), two IR-active optical modes (A_{2u} and E_{1u}) and the rest (B_{1u} , E_{2u} and $2B_{2g}$) are optically inactive (silent) modes.^{121,}

¹²² The Raman tensors of the E_{2g} , E_{1g} and A_{1g} modes have the following forms:

$$\begin{aligned} A_{1g} &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \\ E_{1g} &: \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix} . \\ E_{2g} &: \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

Similarly, rhombohedral structured bulk Bi_2X_3 (X=Se, Te) belongs to the space group D_{3d}^5 ($R\bar{3}m$), and the primitive unit cell overruns three QLs (five atoms), as shown in Figure 1-5a. Consequently, there are 15 Γ phonon modes, three acoustic modes and twelve optical modes. The irreducible representations of the phonon modes are shown as $\Gamma_{\text{bulk}} = 3E_u + 3A_{2u} + 2E_g + 2A_{1g}$, among which $2E_g$ and $2A_{1g}$ are Raman-active, $2E_u$ and $2A_{2u}$ are IR-active, and the rest three are acoustic phonon modes (E_u and A_{2u}).¹²³ The Raman tensors of the E_g and A_{1g} modes can be written as

$$\begin{aligned} A_{1g} &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \\ E_g &: \begin{pmatrix} c & d & 0 \\ d & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & c \\ d & c & 0 \end{pmatrix} . \end{aligned}$$

In both transition metal dichalcogenide and bismuth chalcogenide systems, the two-fold degenerate E modes describe the in-plane (shear) lattice vibrations, and the non-degenerate A symmetry modes represent the vibrations in the out-of-plane (breathing) direction along

the z -axis. The displacement schematics of these Raman-active and IR-active optical phonon modes are displayed in Figure 1-7, where the unit cell of 2 TLs is chosen for the MX_2 system. For Bi_2X_3 , the vibrations are displayed within one QL, which is equivalent to within the rhombohedral polyhydron unit cell as displayed in Figure 1-5a. The arrow indicates the vibration direction and its length is proportional to the displacement magnitude. Note that only one schematic is shown for the two-fold degenerate E modes, and the other one is vibrating with the same manner while out of the paper plane. The superscript in the phonon notation, as in E_{2g}^1 and E_{2g}^2 is to distinguish the two different phonon modes that belong to the same irreducible representation E_{2g} in the material. Besides the Γ phonon modes, the phonon dispersions along the high-symmetry points in the Brillouin zone have also been calculated for both systems.^{124, 125}

Figure 1-7 Vibrational schematics of the Raman-active and IR-active optical phonon modes in bulk (a) 2H-MX₂ and (b) Bi₂X₃.

Raman and IR spectroscopy have been extensively used to study the phonon properties in these layered materials, and the optical phonon modes displayed in Figure 1-8 have been identified in their bulk crystals. The four Raman-active modes E_{2g}^2 , E_{1g} , E_{2g}^1 and A_{1g} in 2H-MoS₂ have been observed at around 34 cm⁻¹, 287 cm⁻¹, 383 cm⁻¹ and 409 cm⁻¹,

respectively, with different polarization dependences.^{122, 126} The detailed Raman selection rules will be discussed in Chapter 2.4. The two IR-active modes E_{1u} and A_{1u} were also identified around 384 cm^{-1} and 470 cm^{-1} through IR reflectivity measurements.¹²² Note that the Raman-active E_{2g}^1 mode and the IR-active E_{1u} mode have very close frequencies, which can be reflected in their vibrational schematics where the vibrations within each TL are the same while the inter-TL vibrations have different phases. The weak interlayer vdW force results in only slight difference in the frequencies of these two modes, as experimentally demonstrated, and the two modes will be degenerate in frequency without the interlayer interactions. Such a pair of modes are normally referred to as Davydov doublets. Besides the E_{2g}^1 and E_{1u} doublets, there exist many other conjugate pairs such as the Raman-active E_{2g}^2 mode and the acoustic E_{1u} mode, B_{2g} (silent) and E_{1u} (acoustic), E_{1g} (Raman) and E_{2u} (silent), A_{1g} (Raman) and B_{2u} (silent), A_{2u} (IR) and B_{2g} (silent). The frequency difference between the two conjugate modes varies from pair to pair. In general, a lower mode frequency corresponds to a larger difference. For example, the frequency difference is up to 34 cm^{-1} in the E_{2g}^2 and E_{1u} pair. Note that the formation of Davydov doublets is a generic phenomenon in layered MX_2 materials and is completely attributed to the weak interlayer vdW interactions. According to the group theory analysis, the phonon properties in MoSe_2 , WS_2 , WSe_2 are the same as in MoS_2 , and the only difference is the absolute phonon frequencies. In principle, a larger molecular weight would result in a smaller frequency. For instance, the A_{1g} mode in MoS_2 is around 409 cm^{-1} , while it is around 250 cm^{-1} in WSe_2 .

In bismuth chalcogenides, the four Raman-active phonon modes E_g^1 , A_{1g}^1 , E_g^2 and A_{1g}^2 have been identified through Raman spectroscopy at around 37 cm^{-1} , 62 cm^{-1} , 102 cm^{-1} and 134 cm^{-1} , respectively, for bulk Bi_2Te_3 ,¹²⁷ and at around 37 cm^{-1} , 72 cm^{-1} , 137 cm^{-1} and 174 cm^{-1} , respectively, for bulk Bi_2Se_3 .^{123, 128} The vibration symmetries of these Raman-active modes can be reflected by polarized Raman measurements, where the symmetry selection rule plays the key role in depending on the scattering geometry as well as the Raman tensors of the phonon modes (see Chapter 2.4.2 for details). The four IR-active

modes E_u^1 , E_g^1 , E_u^2 and E_g^2 in Bi_2Te_3 were observed around 50 cm^{-1} , 94 cm^{-1} , 95 cm^{-1} and 120 cm^{-1} , respectively, through IR reflectivity measurements at room temperature.¹²³ In bulk Bi_2Se_3 crystals, however, only the E_u^1 and E_u^2 modes have been experimentally identified around 65 cm^{-1} and 129 cm^{-1} .¹²³ The spin-orbit coupling effect in Bi_2X_3 not only accounts for their intriguing topological insulating properties, but also largely affects the phonon properties. Through *ab initio* calculations, Cheng *et al.* found that the frequencies of the in-plane vibrational E modes change a lot with and without the consideration of the spin-orbit coupling, while those of the out-of-plane A modes exhibit less dependence.¹²⁹ Their calculations also show that better agreement between experiments and calculations can be achieved without considering the spin-orbit coupling effect. Comprehensive investigations on the lattice dynamics in bismuth chalcogenides were conducted through neutron scattering,¹²³ from which phonon dispersions along the out-of-plane c axis as well as along the bisectrix ($\Gamma \rightarrow A$) were obtained, agreeing well with the Raman scattering and IR reflectivity studies.

Figure 1-8 Raman spectroscopy of MoS_2 and Bi_2Se_3 2D crystals. (a) Stokes Raman spectra of 1-6TL and bulk MoS_2 . The frequency evolution of the E_{2g}^1 and A_{1g} modes with varying

thickness is shown in (b).¹³⁰ (c) Stokes and anti-Stokes Raman spectra of 6-16 QL and bulk Bi₂Se₃ and the A_{1g}^1 peak is shown in the zoom-in spectra on the right.¹²⁸ (d) Thickness dependence of the A_{1g}^1 peak extracted from (c).¹²⁸

Phonon properties in 2D crystals are closely related to those of their bulk counterparts, and they also are intrinsically different. Firstly of all, from the symmetry point of view, the crystal symmetry is changed from 3D to 2D, which, correspondingly results in different phonon symmetries and optical activities. Secondly, due to the large surface-to-volume ratio, surface conditions will largely influence the phonon properties in 2D crystals. Theoretical calculations on both the MX₂ and the Bi₂X₃ systems predict that the frequencies of the phonon modes are different from bulk to monolayers.^{124, 129} The first experimental demonstration on the dimensionality-dependent phonon properties was realized on 1-6TL and bulk MoS₂ by Lee *et al.* through Raman spectroscopy, as shown in Figure 1-8a.¹³⁰ The A_{1g} and E_{2g}^1 modes in bulk exhibit redshift and blueshift, respectively, with decreasing thickness. Figure 1-8b shows the thickness-dependent phonon frequencies of these two Raman peaks extracted from Figure 1-8a and their frequency difference, which is widely adopted for the fast and convenient determination of 2D MoS₂ crystal thickness below 4 TLs. The redshift of the A_{1g} mode with decreasing thickness can be intuitively understood as a phonon softening effect caused by less vdW restoring force in thinner samples; the anomalous blueshift of the E_{2g}^1 mode is attributed to the long range Coulomb interactions.^{130, 131} Besides the most phonon frequency change, the linewidth of the phonon peaks also shows distinct thickness dependence and in general broadening from 3D to 2D. Similar phonon behaviors have also been reported in other transition metal dichalcogenides such as WS₂, WSe₂ and MoSe₂ 2D crystals.^{57, 132} The phonon modes in Bi₂X₃ exhibit similar frequency and linewidth change from 3D to 2D. Zhang *et al.* reported the Raman spectroscopy on 6-16QL Bi₂Se₃ nanoplates synthesized through wet chemistry.¹²⁸ As shown in Figure 1-8c, the A_{1g}^1 mode in bulk shows a frequency softening with decreasing thickness, similarly with the A_{1g} mode behavior in MoX₂. The frequency shift of the A_{1g}^1 peak can be quantitatively explained by the uncertainty principle and phonon dispersion

relation (refer to Chapter 2.6). Moreover, Wang *et al.* reported new Raman peaks in MBE grown 1-7QL Bi₂Te₃ thin films, one of which they assigned to a surface phonon mode.¹³³

1.4 Motivation and Objectives of this Thesis

2D crystals beyond graphene represent a wealth of opportunities for investigating novel physics as well as advancing new technologies. A deep understanding of the lattice dynamics in 2D crystals, is not only essentially important from the fundamental physics point of view, but also indispensable for studying and engineering their optical and electronic properties through electron phonon interactions. The phonon properties of the layered bulk crystals have been studied for decades, while the phonon behaviors in the 2D regime have not been comprehensively understood yet, in spite of some existing theoretical and experimental investigations. The objective of this thesis is to gain a full picture of the lattice vibrations in the layered 2D crystals, by investigating the phonon properties in the transition metal dichalcogenide and bismuth chalcogenide systems, through a combination of Raman spectroscopy, first principles calculations and group theory analysis. More specifically, this thesis is trying to address four major issues: (1) What are the intrinsic phonon properties, in terms of the quantity, symmetry, and optical activity of the phonon normal modes, in a 2D crystal with given thickness? (2) How to assign the Raman peaks or features in a Raman spectrum, and how to interpret their polarization dependence? (3) How do the phonon normal modes correlate in crystals with different symmetries, sizes, and dimensionalities? (4) What governs the frequency, intensity, linewidth and lineshape evolution of the Raman features as a function of thickness and dimensionality? By revealing these answers, we hope to shed light on a general understanding of the lattice dynamics in layered materials from 3D to 2D.

1.5 Organization of the Thesis

Besides the general introduction in this chapter to the optical, electronic, as well as lattice vibrational properties of the layered transition metal and bismuth chalcogenide 2D crystals, the rest of this thesis is organized as follows:

Chapter 2 gives a systematic introduction to Raman spectroscopy. It starts with the basic concepts of the Raman scattering within the context of different scattering effects, followed by a brief introduction to its classical and quantum theories. Then we put the Raman scattering effect in the frame of spectroscopy, where the characteristics of Raman spectra and the Raman selection rules are introduced. Resonant Raman scattering is also discussed in this chapter in terms of its quantum theory and some experimental characteristics, to support some of our results in the later chapters. Moreover, the concept of phonon confinement effect is introduced, which is commonly present in the Raman spectroscopy of 2D crystals. Moreover, the micro-Raman spectrometer we used for the Raman and photoluminescence measurements is introduced, in addition to some techniques we developed for the ultralow frequency Raman spectroscopy.

Chapter 3 mainly focuses on the sample preparations and characterizations involved in later studies. Transition metal dichalcogenide 2D crystals (MoS_2 , MoSe_2 , WS_2 , WSe_2) are prepared through mechanical exfoliation, and bismuth chalcogenide 2D crystals (Bi_2Te_3 , Bi_2Se_3) are synthesized through a vapor transport method. Since the synthesis of ultrathin Bi_2Te_3 and Bi_2Se_3 crystals is not trivial, detailed investigations on their optical contrast, growth mechanism, and electron transport properties are conducted.

Chapter 4 reveals the presence of interlayer breathing and shear phonon modes in the transition metal dichalcogenide 2D crystals. Four series of Raman peaks with different frequency evolution trends as a function of crystal thickness were observed through ultralow frequency ($<50 \text{ cm}^{-1}$) Raman spectroscopy, which were successfully assigned to the interlayer vibrational modes with the support of first principle calculations and group theory analysis. The behavior of the interlayer vibrational modes in 2D crystals demonstrates the important role played by the crystal symmetry and dimensionality in governing the phonon properties.

Chapter 5 focuses on the high frequency Raman spectroscopy on the transition metal dichalcogenide 2D crystals. The anomalous lattice vibrations (blueshift of the mode and redshift of the mode with decreasing crystal thickness) are observed in all the four MX_2 (MoS_2 , MoSe_2 , WS_2 , WSe_2) crystals, and were attributed to the competition between the surface effect and the thickness effect, based on the first principles calculations. Besides, unexpected new Raman peaks are resolved in few-TL WSe_2 , which is a result of the lower symmetry and dimensionality of the 2D crystals compared to the 3D bulk.

Chapter 6 systematically investigates the lattice dynamics in Bi_2Te_3 and Bi_2Se_3 2D crystals through polarized Raman spectroscopy, group theory analysis and first principles calculations. Ultralow frequency interlayer breathing and shear modes are observed for the first time in the 2D crystals, which however is strictly excluded in the bulk crystals due to a higher crystal symmetry. Besides the intrinsic interlayer vibrational modes, another ultralow frequency ($<20\text{ cm}^{-1}$) interface mode is revealed in Bi_2Te_3 2D crystals, which is originated from the interface interactions between the substrates and Bi_2Te_3 crystals. The frequency and linewidth evolutions of the high frequency Raman peaks are also uncovered, which can be interpreted through the phonon confinement effect.

In the end, a summary of the whole thesis and a brief outlook on the future research of the layered metal chalcogenide 2D crystals is given in Chapter 7.

Chapter 2 Raman Spectroscopy

2.1 Basic Concepts of Raman Scattering

Light scattering is an important photophysical phenomenon, in addition to optical reflection, transmission, and absorption when shining light onto a material. The scattering of light can be considered as the redirection of light when encountering an obstacle or inhomogeneity. Light scattering is a microscopic light-matter interaction process, instead of simply being light “bouncing” off an obstacle. When the incident light (electromagnetic wave) interacts with the material, the electrons within will get perturbed and oscillate. The perturbation and oscillation of the electron clouds would in turn induce electromagnetic wave radiation. The majority of the scattered light has the same energy as the incident light, which is elastic scattering and also known as Rayleigh scattering. While a small fraction of the incident light could experience an energy gain or loss during the scattering process, this is called inelastic scattering and commonly referred to Raman scattering and Brillouin scattering.

Inelastic scattering effects provide exceedingly useful tools to study the fundamental excitations in molecules and crystals. The foundation of inelastic light scattering can be traced back to almost one century ago when it was firstly predicted by Brillouin in 1922 through long wavelength elastic waves.¹³⁴ Brillouin scattering effects are commonly based on the low frequency excitations in a material, such as the acoustic phonons, magnetic spin waves (magnons), and a lot of other quasiparticles.¹³⁵ In 1923, Smekal developed a theory of inelastic light scattering through a two energy system,¹³⁶ whose essential characteristics are captured by the experimental phenomena discovered in 1928 by Raman in liquids,¹³⁷ and also independently by Landsberg and Mandelstam in crystals.¹³⁸ This inelastic scattering effect is commonly attributed to the Indian scientist Sir Chandrasekhara Venkata Raman and named after him as Raman scattering effect. Different from Brillouin scattering, Raman scattering reveals slightly higher energy levels of excitations-the vibrations and rotations in molecules, optical phonon modes in crystals, magneto excitons, charge density waves, plasmons, magnetic transitions, *etc.*¹³⁵ In this thesis, we will focus on the Raman scattering of optical phonons in crystals.

Raman scattering can be divided into two processes, Stokes and anti-Stokes scatterings, corresponding to the energy loss and gain situations, respectively. Figure 2-1 schematically shows the Raman scattering processes of a phonon. The Stokes Raman scattering refers to the transition process of an electron from the ground vibrational state to an intermediate (virtual) state and then back to an excited vibrational state. The energy loss of the scattered photon $\Delta\nu$ corresponds to the energy of the phonon involved in the scattering process. Similarly, the anti-Stokes Raman scattering refers to the transition of an electron from an excited vibrational state to the intermediate (virtual) state and then back to the ground vibrational state. The energy gain of the scattered photon is again equal to the phonon energy $\Delta\nu$, which could also be reflected in the IR absorption process. A phonon can be considered as created during the Stokes process and annihilated during the anti-Stokes process, while no phonons are involved in the process of Rayleigh scattering. Note that Figure 2-1 only shows the simplest first-order and non-resonant situation for Raman scattering. In principle, high-order (multi-phonon) Raman scattering could also occur, especially in resonant conditions, where the intermediate states of the optical transitions become real electronic states. Resonant Raman scattering will be discussed in detail in later sections of this chapter.

Figure 2-1 Schematic of Raman scattering, Rayleigh scattering, and IR absorption processes.

The efficiency of scattering can be characterized by the cross section σ . In experiments, the scattered signal is usually collected in a certain direction within a certain solid angle

($\delta\Omega$) and a certain frequency range ($\delta\omega_s$) centered at ω_s . Therefore, differential cross section $\frac{\partial\sigma}{\partial\Omega\partial\omega_s}$ should be more appropriate for the discussion of Raman scattering intensities.¹³⁹ In a crystal, the differential Raman cross section depends on the frequency and polarization of the incident photon, as well as the orientation of the crystal and the symmetry of the phonon mode. In general, the cross section of Raman scattering is several orders smaller than that of Rayleigh scattering, and the probability of an incident photon being Raman scattered is approximately only 10^{-7} . The small cross sections of Raman scattering limited the early experimental studies after its discovery in 1928. The advent of lasers in 1960 drastically stimulated the research on Raman scattering effect and the development of Raman spectroscopy. Powerful lasers, with their monochromaticity, wide range frequency selectivity, coherence, and collimation, led to the discovery and study of more inelastic scattering phenomena like the resonant Raman scattering and stimulated Raman scattering.¹³⁵

2.2 Theory of Raman Scattering

The Raman scattering effect, in terms of the photon energy change during the inelastic scattering process, can be explained within the framework of classical electromagnetism. The classical description is commonly used for introducing the basic concepts of Raman scattering. While for a quantitative description of the scattering intensities, quantum mechanics needs to be involved. The quantum theory of Raman scattering provides a comprehensive picture of the scattering process, and is essential for the understanding of resonant Raman scattering, electron-phonon interaction, phonon-phonon interaction, *etc.*

2.2.1 Classical Description

In classical electromagnetism, an external electric field would cause the charge redistribution within a material, like the deformation of the electron clouds and the displacement of the nuclei. The tendency of the charge redistribution responding to the external field is characterized by the electric polarizability $\tilde{\alpha}$, which is intrinsically related

to the dielectric constant and susceptibility of the material. Light scattering can be understood simply through the concepts of electric dipole formation and radiation.^{118, 140}

During Raman scattering, the presence of external electromagnetic field (incident photon) can cause electric polarization to occur within the crystal. When the external field is weak, as is often the case in Raman scattering experiments, the induced dipole moment $\vec{P}$ is proportional to the electric field $\vec{E}$

$$\vec{P} = \tilde{\alpha} \cdot \vec{E} \quad (2-1)$$

where the polarizability $\tilde{\alpha}$ is a second-rank tensor. The lattice vibrations of the crystal will modulate the polarizability. Considering the modulation of a phonon mode with frequency ω_q , the polarizability of the crystal becomes

$$\tilde{\alpha} = \tilde{\alpha}_0 + \tilde{\alpha}_1 \sin \omega_q t, \quad (2-2)$$

where $\tilde{\alpha}_0$ is the polarizability when the nuclei are at the equilibrium positions, and $\tilde{\alpha}_1 \sin \omega_q t$ is the polarizability change induced by the lattice vibration. The electric field of the incident light is oscillating at a frequency ω_i with an amplitude of $\vec{E}_0$

$$\vec{E} = \vec{E}_0 \sin \omega_i t. \quad (2-3)$$

Therefore the induced dipole moment by the optical field can be written as

$$\begin{aligned} \vec{P} &= \vec{E}_0 (\tilde{\alpha}_0 + \tilde{\alpha}_1 \sin \omega_q t) \sin \omega_i t \\ &= \vec{E}_0 \left[\tilde{\alpha}_0 \sin(\omega_i t) + \frac{1}{2} \tilde{\alpha}_1 \cos(\omega_i - \omega_q)t - \frac{1}{2} \tilde{\alpha}_1 \cos(\omega_i + \omega_q)t \right]. \end{aligned} \quad (2-4)$$

Equation (2-4) indicates that there exist three frequencies of light that will be radiated from the dipole oscillation. The first term of the equation refers to the Rayleigh scattering, where the scattered light possesses the same frequency ω_i as the incident light. The second and third term represent the inelastic scattering, where the frequency of the scattered light is downshifted or upshifted by a magnitude of ω_q from the incident frequency, corresponding to the Stokes and anti-Stokes Raman scattering processes.

The light scattering intensity follows a ω_s^4 dependence according to the classical electrodynamics, where ω_s represents the frequency of the scattered light.¹⁴¹ It is known that electromagnetic radiation will occur when the electric charges experience acceleration, and the radiated electric field is therefore proportional to the second time derivative of the dipole moment. For an sinusoidal oscillating electric dipole $P_0 \sin(\omega t)$, we have the radiated field $E \propto \frac{\partial^2 P}{\partial^2 t} \propto \omega^2$. The intensity of the radiation is therefore $I \propto E^2 \propto \omega^4$. This fourth power dependence of scattering intensity on frequency is applicable for both elastic and inelastic scattering. In fact, this explains why the sky appears blue, since the Rayleigh scattering of blue light is stronger than the red light. For Raman scattering, since the phonon frequencies are much smaller than that of the photons, the incident light and scattered light can be considered to have the same energy approximately $\hbar\omega_i \approx \hbar\omega_s$. According to the ω_s^4 dependence, the absolute Raman intensity should increase with E_{laser}^4 . Strictly speaking, the Stokes scattering is supposed to be slightly weaker than the anti-Stokes scattering, since the frequency of Stokes scattered light is $2\omega_q$ smaller than the anti-Stokes frequency. However, it is often the other way around for non-resonant Raman scattering, revealing the limitation of the classical theory.

2.2.2 Quantum Description

The main goal of the quantum mechanical theory of Raman scattering is to obtain a quantitative description for the Raman intensities, which can be handled within the framework of the time-dependent perturbation theory and developed from Fermi's golden rule.

In quantum physics, Fermi's golden rule describes the transition probabilities from one energy state to another, due to a time-dependent perturbation. According to Fermi's golden rule, the transition probability per unit time from an initial state i to a final state f is

$$W \cong \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \rho_f, \quad (2-5)$$

where H' is the Hamiltonian of a time-dependent perturbation, and ρ_f is the density of final states.¹¹⁸ As described by equation (2-5), if the initial (or final) state is a discrete level (such as an impurity state) and the final (or initial) state is a continuum (such as the valence and conduction bands), the transition probability only depends on the density of the initial (or final) states. If both the initial and final states are continuum, ρ_f represents the joint density of states. Fermi's golden rule describes the first-order transition processes that can be derived from the first-order perturbation theory.

One-phonon Raman scattering in crystals normally include three transition processes and need to be described using the third-order perturbation theory, where the physics behind is the same as presented by equation (2-5). The Hamiltonian of the Raman scattering event can be written as

$$\begin{aligned} H &= H_0 + H' \\ &= (H_e + H_L + H_R) + (H_{eR} + H_{eL}), \end{aligned} \quad (2-6)$$

where H_e , H_L , and H_R are the Hamiltonians of electrons, phonons (lattice vibrations), and photons (radiations), respectively. The interaction between electrons and photons H_{eR} , and the interaction between electrons and phonons H_{eL} , function as the perturbation term. The interaction between photons and phonons H_{LR} is negligible since the nuclei are too heavy to be perturbed by weak electromagnetic field. The process of first-order Raman scattering can be treated as follow: After absorbing an incident photon ($\hbar\omega_i$), an electron transits from the initial state (i) to an intermediate state (m), then it gets scattered to another intermediate state (m') through the scattering of a phonon, in the end, the electron transits back to a final state (f) with the emission of a photon ($\hbar\omega_s$). These basic transition processes can be simply displayed in Figure 2-2a, as well as the Feynman diagrams^{118, 142} (Figure 2-2b).

The Fermi's golden rule can be used for each transition process. For example, the first transition from the initial state (i) to the intermediate state (m) contributes a term to the

scattering probability per unit time in a form of $\frac{\langle m | H_{eR}(\omega_i) | i \rangle}{[\hbar\omega_i - (E_m - E_i)]}$, with ω_i being the

frequency of the incident photon, and E_i , E_m being the energy levels of the initial and intermediate states. Similarly, the contribution from the second transition process ($m \rightarrow m'$) has an energy dominator of $\hbar\omega_i - (E_m - E_i) - \hbar\omega_L - (E_{m'} - E_m) = \hbar\omega_i - \hbar\omega_q - (E_{m'} - E_i)$. For the third process, the dominator is $\hbar\omega_i - \hbar\omega_L - \hbar\omega_s - (E_f - E_i)$ and becomes a δ function $\delta(\hbar\omega_i - \hbar\omega_q - \hbar\omega_s)$, since the final and initial states are the same ($f = i$). Overall, the first-order Raman scattering probability per unit time can be obtained as:

$$W(\omega_s) = \frac{2\pi}{\hbar} \left| \sum_{m,m'} \frac{\langle i | H_{eR}(\omega_s) | m' \rangle \langle m' | H_{eL} | m \rangle \langle m | H_{eR}(\omega_i) | i \rangle}{[\hbar\omega_i - (E_m - E_i)] [\hbar\omega_i - \hbar\omega_L - (E_{m'} - E_i)]} \right|^2 \times \delta(\hbar\omega_i - \hbar\omega_L - \hbar\omega_s). \quad (2-7)$$

Figure 2-2 only depicts the simplest and most intuitive first-order Raman scattering process. Depending on the order of the three transition events, there could be in total six different Feynman diagrams. For non-resonant Raman scattering, all the six possible processes could contribute to the total scattering intensity. While in the resonant conditions with a fixed energy between the conduction and valence bands, only the process described by Figure 2-2 will dominate. Therefore, equation (2-7) is enough for the calculation of Raman intensities under resonant conditions, which will be discussed later.

Figure 2-2 (a) Schematic of one-phonon Raman scattering process and (b) the corresponding Feynman diagram. ω_i and ω_s are the frequencies of the incident light (laser) and scattered light, and ω_L is the frequency of the phonon involved in the scattering.

2.3 Characteristics of Raman Spectra

2.3.1 Raman Spectral Lineshape and Linewidth

A Raman spectrum is a plot of the scattered light intensity I_s as a function of the wavenumber difference between the incident and scattered light ($q_i - q_s$), as shown in Figure 2-3. The wavenumber defined here is the inverse of wavelength $q = \frac{1}{\lambda}$. The energy axis of a Raman spectrum is called Raman shift and displayed in the unit of cm^{-1} , since the phonon wavelengths are in the order of cm . The Stokes and anti-Stokes Raman spectra are displayed on the positive and negative energy sides, respectively, and the scattered phonons are shown as peaks at $\pm q_{ph}$. 0 cm^{-1} represents the Rayleigh scattering and it would normally shows as a steep rise in the vicinity of 0 cm^{-1} since Rayleigh scattering is much stronger than Raman scattering.

Figure 2-3 Schematic of a typical Stokes and anti-Stokes Raman spectrum.¹¹⁸

A phonon peak in a Raman spectrum mostly exhibits a Lorentzian lineshape. This can be understood by treating phonon excitation as a harmonic oscillator damped by interactions with other excitations in the same medium such as heat, impurities, *etc.*¹¹⁸ Consider a harmonic oscillator with eigen frequency ω_{ph} being damped with a damping constant γ , the frequency of the oscillator will lose its monochromaticity since the

oscillation amplitude gradually decreases. In the limit of weak damping ($\omega_{ph} \gg \gamma$), the frequency distribution of the damped harmonic oscillator follows a Lorentzian function

$$I(\omega) = \frac{I_0}{\pi} \cdot \frac{\gamma}{(\omega - \omega_{ph})^2 + \gamma^2}, \quad (2-8)$$

where the center locates at ω_{ph} with intensity I_0 , and the full width half maximum (FWHM) is 2γ . The finite linewidth (2γ) of the Raman peak indicates an uncertainty of the phonon energy, which corresponds to a finite phonon lifetime, according to the uncertainty principle $\Delta E \cdot \Delta t \sim \hbar$. The main contribution to the finite phonon lifetime is the anharmonicity of the potential for the phonon, phonon-phonon scattering, as well as electron-phonon interaction.¹¹⁸ A longer phonon lifetime here means a slower damping rate and a smaller spectral linewidth of the Raman peak. Therefore, γ is inversely proportional to the phonon lifetime and a Raman spectrum in this way can provide information on the lifetime of a phonon mode through its linewidth.

In some specific cases, a Raman peak can deviate from the simple Lorentzian shape. One example is when a Raman feature is contributed by the scattering of several phonons, with different frequencies and weight. This phonon convolution can be analyzed by multi-Lorentzian fitting. Electron-phonon interaction can also cause the lineshape change of a Raman peak, which might become asymmetric. A good example is the Breit-Wigner-Fano (BWF) lineshape when the discrete phonon states interfere with a continuum of electronic states, given by

$$I(\omega) = I_0 \frac{[1 + (\omega - \omega_0)/q\gamma]^2}{1 + [(\omega - \omega_0)/\gamma]^2}, \quad (2-9)$$

where the parameter q defines the degree of the peak asymmetry and a smaller value of $|q|$ causes the peak to be more asymmetric. The peak frequency the BWF lineshape is $\omega_0 + \frac{\gamma}{q}$, and the FWHM becomes $2\gamma \cdot \left| \frac{q^2 + 1}{q^2 - 1} \right|$. In the limit of weak electron-phonon interaction ($q \rightarrow \infty$), equation (2-9) is reduced to a Lorentzian lineshape. Such electron-phonon interaction caused BWF lineshape has been observed in graphene and Bi₂Se₃ 2D

crystals.^{128, 143} Moreover, phonon confinement can also result in the lineshape and linewidth change of a Raman peak, as will be discussed later in this thesis.

2.3.2 Stokes and Anti-Stokes Spectra

While the Stokes and anti-Stokes spectra are symmetric in terms of the Raman peak frequencies, the intensities of the peaks are different on both sides, as shown in Figure 2-3. Raman intensities directly depend on the probabilities of the scattering processes.

The probability of creating (Stokes process) and annihilating (anti-Stokes process) a phonon is determined by the phonon statistics, which is given by the Bose-Einstein distribution function:

$$\langle n \rangle = \frac{1}{e^{\hbar\omega_{ph}/k_B T} - 1}. \quad (2-10)$$

Here, $\langle n \rangle$ is the average number of phonons with frequency ω_{ph} at a given temperature T . The creation of a phonon means the phonon number goes from $\langle n \rangle$ to $\langle n+1 \rangle$, whose probability is proportional to $\langle n+1 \rangle$; while for the time-reversed process, the annihilation of a phonon goes from $\langle n+1 \rangle$ to $\langle n \rangle$, with a probability proportional to n . Recall that in section 2.2.1, the intensity of the scattered light follows a ω^4 dependence, the intensity ratio for the Stokes and anti-Stokes scattering becomes

$$\frac{I_S}{I_{aS}} \propto \left(\frac{\omega_S}{\omega_{aS}} \right)^4 \cdot \frac{\langle n+1 \rangle}{\langle n \rangle} \propto \left(\frac{\omega_i - \omega_{ph}}{\omega_i + \omega_{ph}} \right)^4 \cdot e^{\hbar\omega_{ph}/k_B T}, \quad (2-11)$$

where I_S and I_{aS} denote that Raman intensities of the given Stokes and anti-Stokes peaks,

respectively, and ω_i is the frequency of the incident laser.¹³⁹ While $\left(\frac{\omega_i - \omega_{ph}}{\omega_i + \omega_{ph}} \right)^4$ is slightly

smaller than 1, $e^{\hbar\omega_{ph}/k_B T}$ is much larger than 1 for most phonons at or below room temperature, which explains why Stokes Raman peak is usually stronger than the anti-Stokes peak. Note that equation (2-11) is derived based on the time reversal symmetry. Strictly speaking, the relation only holds when the incident laser frequency for the Stokes

process matches the scattered frequency for the anti-Stokes process, and also the incident laser frequency for the anti-Stokes process matches the scattered frequency for the Stokes process. The Stokes and anti-Stokes processes excited by the same laser also approximately follow this relation since their frequencies are very close.

Equation (2-11) provides a way to determine the sample temperature through the Stokes and anti-Stokes intensity ratio, given a reference relation between the sample temperature and Raman spectra. However, this equation does not apply to the resonant Raman scattering for I_s and I_{as} obtained by the same laser, since the resonant conditions might vary a lot for the Stokes and anti-Stokes processes.¹¹⁸

2.4 Raman Selection Rules

2.4.1 Energy and Momentum Conservation

During Raman scattering, both energy and momentum should conserve for the involved quasiparticles (photons and phonons). For the first-order Raman scattering, we have

$$\begin{aligned}\hbar\omega_i &= \hbar\omega_s \pm \hbar\omega_{ph} \\ \hbar k_i &= \hbar k_s \pm \hbar k_{ph}\end{aligned}, \quad (2-12)$$

where ω and k are the angular frequency and wave vector of the incident photon (i), scattered photon (s) and phonon (ph). The positive and negative signs represent the Stokes and anti-Stokes processes, respectively. In Raman measurements, there is often an angle θ between the incident light and the detector, as shown by the left graph of Figure 2-4. According to equation (2-12), the wave vector of the phonon becomes:

$$k_{ph}^2 = k_i^2 + k_s^2 \pm 2k_i k_s \cos \theta. \quad (2-13)$$

The lasers used for Raman measurements are mostly in the range from near-ultraviolet to IR (1~4 eV), and the wave vectors ($k = \frac{2\pi}{\lambda}$) are on the order of 10^5 cm^{-1} . Since the incident and scattered photons have very small energy difference (several orders smaller

than the photon energy), the magnitudes of their wave vectors remain almost the same. Therefore, the wave vector of the phonon involved in the Raman scattering should be either on the order of 10^5 cm^{-1} or smaller, depending on θ . The size of the Brillouin zone, however, is on the order of $10^7\text{-}10^8 \text{ cm}^{-1}$, much larger than the phonon wave vectors. Therefore, we can conclude that only the phonons near the Brillouin zone center (Γ point), also known as the long-wavelength phonons can be involved in Raman scattering. To detect phonons far away from the Brillouin zone center through inelastic scattering, X-ray and fast neutrons with energy far above 1 eV are needed.

Figure 2-4 Configuration of Raman scattering measurements (left) and the wave vector relations for the Stokes (middle) and anti-Stokes processes (right).

2.4.2 Symmetry Selection Rule

Besides the $k \approx 0$ rule discussed above, Raman scattering of phonons has to obey certain symmetry selection rules, that is to say, only phonons with certain vibrational symmetries can be scattered. Recall that in the classical picture, the modulation of the electric polarizability through lattice vibrations is used for explaining Raman scattering. Simply speaking, only those vibrations that would cause a polarizability change are Raman-active. The symmetry of a Raman-active phonon mode can be characterized by a second-rank 3×3 tensor $\tilde{R}$, known as the Raman tensor. The Raman tensor $\tilde{R}$ is closely related to the electric polarizability tensor $\tilde{\alpha}$ with the relation

$$\tilde{R} = \frac{\partial \tilde{\alpha}}{\partial Q} Q, \quad (2-14)$$

where both $\tilde{\alpha}$ and $\tilde{R}$ are second-rank tensors, and Q is the vector displacement of a given atom induced by the phonon vibration.^{139, 144} Phonon vibrations that could cause the change of the electric dipole moment are IR-active.¹⁴⁴ Some phonons could be both Raman- and IR-active, while the Raman and IR activities are complementary in a centrosymmetric crystal. Some phonons could be neither Raman- nor IR-active, and these are referred to as optically inactive or silent modes.

The Raman selection rule can also be interpreted through the group theory, which is more practical and commonly used for phonons of crystals. Consider the transition between two states a and b through some interaction H , the transition can occur only when the matrix element $\langle b|H|a\rangle$ does not vanish, which requires that $H|a\rangle$ is not orthogonal to $\langle b|$. Group theory is often invoked to determine if a transition vanishes by symmetry, and this information can be found in the character table for a given symmetry group.¹¹⁸ Firstly, we need to identify the irreducible representations for $\langle b|$, H , and $|a\rangle$. If Γ_b pertains to $\Gamma_H \otimes \Gamma_a$, the matrix element $\langle b|H|a\rangle$ does not vanish by symmetry. Recall that in the quantum description of Raman scattering, three transition processes are involved in the first-order scattering, written as $\langle i|H_{eR}(\omega_s)|m'\rangle\langle m'|H_{eL}|m\rangle\langle m|H_{eR}(\omega_i)|i\rangle$ in sequence (equation (2-7)). In order to get a nonzero transition, the irreducible representations of interaction Hamiltonians H_{eR} and H_{eL} have to satisfy the relation

$$\Gamma_1 \subset \Gamma_{H_{eR}} \otimes \Gamma_{H_{eL}} \otimes \Gamma_{H_{eR}}, \quad (2-15)$$

where Γ_1 is the totally symmetric irreducible representation. The electron-photon interaction H_{eR} belongs to the same irreducible representation as the linear basis function x, y, z ; and equation (2-15) is valid only when the electron-phonon interaction H_{eL} pertains to the same irreducible representation as the quadratic basis functions such as xx, yy, zz, xy, yz, xz .¹¹⁸ In practice, the irreducible representations of both basis functions and phonon modes are listed in the character tables for all the 32 point groups. One can identify a phonon mode to be Raman-active if it is corresponding to any quadratic basis functions, which are also reflected as the nonzero Raman tensor elements.

The experimental detection of a phonon mode through Raman scattering not only depends on its optical (Raman/IR) activity, but also on the polarization property of the incident laser as well as the polarization direction chosen for detecting the scattered light. The Raman scattering intensity I is proportional to $|e_i \cdot \tilde{R} \cdot e_s|^2$, with e_i and e_s being the polarization vectors of the incident and scattered light, respectively. A given phonon mode is detectable through Raman spectroscopy only when I has a nonzero value following the equation below¹³⁹

$$I \propto e_i \cdot \tilde{R} \cdot e_s = \begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (2-16)$$

In layered materials, Cartesian axes x , y are defined within the TL plane and z is perpendicular to the plane, along the c -axis. Let us analyse the Raman intensities in 2H-MoS₂/WSe₂ with different polarization configurations. The Raman tensors of the bulk phonon modes are:¹²²

$$\begin{aligned} A_{1g} &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \\ E_{1g} &: \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix} . \\ E_{2g} &: \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

In the most common back scattering geometry, the polarization configurations can be denoted by the Porto notations¹⁴⁵ $\bar{z}(xx)z$ and $\bar{z}(xy)z$, where $\bar{z}$ represents the wave vector of the incident laser beam and z is that of the back scattered signal light. The two symbols in the parenthesis denote the polarizations of the laser light and Raman signal, respectively. The polarization of the scattered light is detected by adding a polarizer in front of the charge-coupled device (CCD). Now equation (2-16) becomes

$$e_i \cdot \tilde{R} \cdot e_s = (x \ 0 \ 0) \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} x \\ 0 \\ 0 \end{pmatrix} \quad (2-17)$$

for the parallel polarization configuration $\bar{z}(xx)z$, and

$$e_i \cdot \tilde{R} \cdot e_s = (x \ 0 \ 0) \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ y \\ 0 \end{pmatrix} \quad (2-18)$$

for the perpendicular polarization configuration $\bar{z}(xy)z$. Substituting the Raman tensors of all the Raman-active modes with their specific forms as shown above, it is found that the E_{2g} mode is detectable under both the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations, while the A_{1g} mode can only be detected under the $\bar{z}(xx)z$ configuration. The E_{1g} mode, however, cannot be observed under either configuration even though it is a Raman-active mode. In order to detect the E_{1g} mode, the polarizations of the incident and scattered light should both have a nonzero z component, according to equation (2-16).

To summarize, the experimental detection of a phonon mode through Raman scattering is determined by the symmetry selection rule, where both the phonon symmetry and the polarization configuration of the scattering geometry are essentially important.

2.5 Resonant Raman Scattering

In the non-resonant Raman scattering theory discussed in section 2.2 of this chapter, only “virtual” intermediate electronic states are involved in the scattering process. In certain cases, real electronic states could function as the intermediate states and affect some of the scattering characteristics, and this special scattering process is referred to as resonant Raman scattering (RRS).

The most distinctive characteristic of resonant Raman scattering is the significant enhancement of the scattering cross section. The Raman scattering probability in the resonant conditions can be characterized by equation (2-7). Here, one of the intermediate

m, m' states (or both) is real electronic states, and one of $E_m - E_i, E_{m'} - E_i$ (or both) represents the real electronic gap between an occupied initial states and an empty intermediate state. When the energy of the incident or scattered photon matches the actual energy gap, the denominator will go to zero and the Raman scattering probability will go to infinity, mathematically. Experimentally, the enhance factor is often around three to six orders. In semiconductors, resonant Raman scattering often happens when the excitation laser energy (E_{laser}) is in the vicinity of the band gap or an exciton energy (E_X). Equation (2-7) now can be written as

$$I(E_{laser}) \propto \left| \frac{A}{(E_{laser} - E_X - i\gamma_r)(E_{laser} - (E_X \pm E_{ph}) - i\gamma_r)} \right|^2, \quad (2-19)$$

where A is a constant and γ_r characterizes the width of the resonance window. γ_r is related to the lifetime of the Raman scattering process, that is, the time delay between the photon absorption and photon emission.¹¹⁸ In other words, γ_r is the inverse of the lifetime of the photoexcited carrier, and is different from the γ in equation (2-8) which is related to the lifetime of the phonon. When varying E_{laser} around the energy E_X , there exist two different resonance conditions: one is when the incident phonon matches the exciton energy $E_{laser} = E_X$, the other is when the scattered photon does $E_{laser} = E_X \pm E_{ph}$. These two conditions are referred to as incoming resonance and outgoing resonance, respectively. Sometimes, these two resonance conditions can be experimentally distinguished as two maxima in the Raman intensity VS. E_{laser} profile, while in most cases they appear as one maximum around $E_{laser} = E_X \pm \frac{1}{2} E_{ph}$.^{135, 139} The effective enhancement of the scattering intensity in RRS are taken advantage of for studying phonons in small samples such as single carbon nanotubes, or samples with very week Raman signals.

Another important feature of RRS is the high-order or multi-phonon scattering, where more than one scattering events occur during the Raman process. The quantum explanation of two-phonon Raman scattering needs to involve the fourth-order perturbation theory and even higher-order for multi-phonon scattering. These high-order processes are much

weaker than the first-order one-phonon scattering and are generally difficult to be observed in non-resonant Raman scattering. In resonant conditions, however, due to the large enhancement of the Raman cross sections, multi-phonon scattering features are likely to appear in the Raman spectra. The $k \approx 0$ rule for one-phonon scattering, according to the energy and momentum conservation, can be relaxed in the multi-phonon scattering process, where instead only $\sum_i k_i \approx 0$ is required, with k_i being the wave vectors of all the phonons involved. In a simple two-phonon scattering process, the two phonons can correspond to the same phonon branch with opposite momenta $\omega_i(k)$ and $\omega_i(-k)$, or two different phonon branches $\omega_i(k)$ and $\omega_j(-k)$. The corresponding Raman shift of this two-phonon scattering could be $\Delta\omega = \pm 2\omega_i$ (Stokes and anti-Stokes second-order modes), or $\Delta\omega = \omega_i \pm \omega_j$ (combination modes). The same rule also applies to multi-phonon scattering. Note that since the phonon wave vectors are not restricted to 0 for the multi-phonon scattering processes, the Raman shift of the high-order or combination modes might not be the same with the frequency sum of phonons that appear in the first-order Raman spectra, due to the phonon dispersion across the Brillouin zone. Similarly, due to the contributions of phonons from the whole Brillouin zone, the high-order or combination peaks are often broadened compared to the first-order Raman peak.

Besides the phonon frequencies directly obtained from the Raman spectra, resonant Raman scattering can also provide rich information on the electron-phonon interaction, electron-radiation interaction and the electronic band structures, as has been extensively exploited in the sp^2 carbon systems, such as carbon nanotubes and graphene, as well as in the classical II-VI and III-V semiconductors, like CdS, GaP, GaSe, ... *etc.*^{118, 135}

2.6 Phonon Confinement Effect in Raman Spectroscopy

The $k \approx 0$ Raman selection rule could be relaxed during the high-order multi-phonon scattering processes, as discussed in the section above. Another situation when the relaxation of this $k \approx 0$ rule could take place is the Raman scattering in crystals with small physical dimensions, where the first-order Raman peaks could exhibit frequency shifts and

broadening compared to their bulk counterparts. This phenomenon is known as the phonon confinement effect in Raman spectroscopy. The phonon confinement effect is a type of quantum size effect that occurs when the phonon wavefunction is confined into a small volume that is on the same magnitude of its wavelength. The origin of the phonon confinement can be understood from the Heisenberg uncertainty principle, according to which the uncertainty of the phonon momentum (Δp) and position (Δx) follows the relation

$$\Delta p \cdot \Delta x \approx h, \quad (2-20)$$

with $\Delta p = \hbar \cdot \Delta k$ and Δx equal to the crystal size ΔL . Equation (2-20) indicates that phonon modes with finite momentum might be involved in the Raman scattering, when the crystal size is significantly decreased.

Figure 2-5 (a) Schematic phonon dispersion curves for the 1D diatom chain. (b) Calculated Raman spectra for the A_{1g}^1 mode in 3D and 2D Bi_2Se_3 .¹²⁸

The frequency shift and broadening of a Raman peak due to the phonon confinement effect can be further depicted by the phonon dispersion relations $\omega(k)$. Figure 2-5a shows the phonon dispersion curves of a simple one-dimensional diatom chain, as discussed in section 1.3.1. For a chain with infinitely large size ($\Delta L \rightarrow \infty$), only the $k \approx 0$ LO phonon denoted with the red circle gets Raman scattered, and the corresponding Raman peak locates at the frequency ω_0 . When the chain length L is sufficiently small, equation (2-20) becomes $\Delta k \cdot \Delta L \approx 2\pi$. In this case, LO phonon modes with wave vectors from 0 to Δk

(denoted by the orange circle) all can be involved in Raman scattering, and the central frequency of the Raman peak would be somewhere between ω_0 and ω_k , depending on the contribution of different phonons. Consequently, the Raman peak will be broadened due to the frequency distribution. In most cases, the phonon dispersion curves bend downwards from the Brillouin zone center to the edge, and the Raman peaks would show redshift in small-sized crystals; while blueshift can also happen if the curves bend upwards.

A quantitative description of the phonon confinement effect in Raman spectroscopy has been developed by Richter, Campbell and Fauchet *et al.* in the 1980's for semiconductor crystallites.^{146, 147} The wavefunction of a phonon with wave vector k_0 in a crystal with size L can be written as

$$\Phi(k_0, r) = W(r, L)e^{-ik_0 r} u(k_0, r) = \Phi'(k_0, r)u(k_0, r), \quad (2-21)$$

where $W(r, L)$ is the phonon weighting function describing the spatial confinement, and $u(k_0, r)$ has the periodicity of the crystal lattice. Through Fourier transformation of $\Phi'(k_0, r)$, we get the Fourier coefficient

$$C(k_0, k) = \frac{1}{(2\pi)^3} \int d^3r \Phi'(k_0, r) e^{-ikr}. \quad (2-22)$$

Equation (2-22) implies that the phonon wavefunction is a superposition of eigenfunctions with a distribution of wave vectors k centered at k_0 . The first-order Raman spectrum can therefore be obtained as

$$I(\omega) = \int \frac{|C(0, k)|^2}{(\omega - \omega(k))^2 + (\gamma_0/2)^2} d^3k, \quad (2-23)$$

with $\omega(k)$ being the phonon dispersion relation and γ_0 the natural linewidth. Note that $\omega(k)$ should normally be anisotropic along different directions in the reciprocal space.

Different shapes of crystallites will determine different forms of $C(0, k)$ and therefore different Raman spectra.¹⁴⁷ A sphere morphology has been adopted for characterizing the Raman spectroscopy of Si and GaAs nanocrystals, where good agreement between calculations and experiments were achieved.^{146, 147} A thin film morphology with only one

dimension confined is appropriate for describing 2D crystals. For a 2D thin film with thickness L , the Fourier coefficients have the following form:

$$|C(0, k)|^2 = e^{-\frac{k^2 L^2}{64\pi^4}} \left| 1 - \operatorname{erf}\left(\frac{ikL}{8\pi\sqrt{2\pi}}\right) \right|. \quad (2-24)$$

According to equation (2-23) and (2-24), Zhang *et al.* calculated the Raman spectra of the A_{1g}^1 mode in Bi_2Se_3 bulk and 2D crystals, as shown in Figure 2-5b, in which the bulk phonon dispersion relation from Γ to Z point was used.¹²⁸ Besides the frequency redshift from bulk to 1QL, the lineshape of the Raman peak deviates from Lorentzian to asymmetric and the deviation is larger with stronger spatial confinement. However, the experimental results exhibit considerable quantitative discrepancies from the calculations, showing the limitation of this phonon confinement model.

2.7 Instrumentation

2.7.1 Introduction to Horiba Jobin Yvon T64000 Spectrometer

All the Raman and photoluminescence spectroscopy measurements in this thesis have been conducted in a commercial triple grating micro-Raman spectrometer (Horiba Jobin Yvon T64000), which is equipped with a liquid nitrogen cooled CCD for the signal detection and the Labspec 6.0 software for data acquisition. Figure 2-6a shows the optical image of our Raman spectroscopy system, where the main components such as the spectrometer, external optics and cryostat for low temperature measurements are shown. One common issue for Raman spectroscopy is the low frequency measurements, due to the strong Rayleigh scattering in the vicinity of 0 cm^{-1} . The traditional combination of a single monochromator and a notch filter normally cannot go beyond 50 cm^{-1} . The Horiba-JY T64000 system, however, has a detection limit as low as 3.5 cm^{-1} through the subtractive configuration of the first two gratings, while the third grating is used to disperse the light. In this section, we focus on introducing the working principle of the Horiba-JY T64000 spectrometer system and the optics to achieve ultralow frequency measurements.

Horiba-JY T64000 spectrometer can operate in a subtractive or additive mode, with different internal optics. The latter is not used in our experiments and therefore will not be discussed in this thesis. Figure 2-6b displays a simplified schematic of the triple grating spectrometer optics working in a subtractive mode. The external laser beam gets reflected into the microscope through a beam splitter (BS) and shines on the sample located below the microscope. The diameter of the beam spot is around 1 μm using a 100 $\times$ objective with a numerical aperture of 0.9. The back scattered signal light is then collected through the microscope and passes the beam splitter, a pinhole, a half waveplate and a polarizer, respectively, before entering the spectrometer through a slit (S1). The size of the pinhole is also adjusted to be 1 μm for confocal measurements. The half waveplates and polarizer are for polarized Raman measurements and can be removed for non-polarized measurements. After passing the entrance slit (S1), the signal light gets reflected onto a grating (G1) by a concave mirror represented by the blue curve and be spatially dispersed. The spatially dispersed signal light then passes another slit (S2) before reaching the second grating (G2). Note that the slit size of S2 is well adjusted to block the light with a frequency very close to the laser line. The spatially dispersed signal light then gets spatially converged by the grating G2 and reaches the third grating (G3) after passing the slit S3, which again disperses the signal light into the CCD. Note that the first two gratings function as a notch filter for stray light while only the third grating serve as the “spectrometer”. Therefore, the first two grating systems are often referred to as the double pre-monochromator, the filtering function of which makes the detection limit of Horiba-JY T64000 spectrometer system as low as 3.5 cm^{-1} . For measurements in the visible or near-IR range, 1800 g/m is normally used for the spectrometer, and 2400 g/mm is employed for the ultraviolet measurements, giving a spectral resolution of around 1 cm^{-1} .

Careful alignment of the spectrometer is essentially important for the low frequency and confocal measurements. A good standard for the optics alignment is that all slits should be kept as small as possible, given that no signal light is blocked. If the laser spot on the sample is around 1 μm , which is often the case when using a 100 $\times$ objective, the pinhole should also be maintained at 1 μm . Consequently, in an ideal condition, the size of S1 and S3 should both be 100 μm . S2 needs to be much larger than 100 μm to let through the spatially dispersed signal light while blocking the laser line and Rayleigh signal. The

optimal size of S2 depends on the wavelength range as well as the groove density of the third grating, and should be carefully adjusted using different excitation lasers. Given a 1800 g/mm G3 with 532 nm excitation, the size of S2 is around 70 mm.

Figure 2-6 (a) Optical image of our Horiba Jobin Yvon T64000 micro-Raman spectrometer system. (b) Schematic of the spectrometer optics in a triple subtractive working mode.

The triple grating Horiba-JY T64000 spectrometer system can also be operated in a single mode, where the first two gratings are bypassed. The external optics is the same for both triple and single mode, the only difference is that the signal light directly goes into the spectrometer after passing the pinhole, half waveplate and polarizer. Without the filtering function of the double pre-monochromator, a notch or edge filter is required for Raman measurements under the single mode and the detection limit is around 50 cm^{-1} - 100 cm^{-1} , depending on the excitation lasers and filters used. The single mode is easy and convenient to use, since it does not require as complicated optical alignment as the triple mode. Moreover, its detection efficiency is several times higher than the triple mode. Ultralow frequency Raman measurements ($< 10 \text{ cm}^{-1}$) have also been demonstrated recently through the combination of a single monochromator with BragGrate notch filters.¹⁴³ The BragGrate notch filters are very costly and currently only available for

limited wavelengths such as 532 nm, 633 nm and 785 nm, *etc.* The double pre-monochromator of the triple mode spectrometer, functions in the same fashion as the BragGrate notch filters, in a wide range from ultraviolet to near-IR, instead of for discrete wavelengths. Therefore, all the measurements in this thesis, have been conducted under triple mode due to its low frequency detection ability in a broad and continuous frequency range.

2.7.2 Filtering of Laser Sidebands

Continuous wave lasers are employed for the Raman spectroscopy studies in this thesis. A broad range of laser frequencies from ultraviolet to near-IR are covered in our lab through a variety of lasers: several solid state lasers (473 nm, 532 nm, 543 nm, 671 nm, 785 nm, 1064 nm); a He-Ne laser (633 nm), a tunable Ar laser with eight discrete frequencies (457 nm, 465 nm, 472 nm, 477 nm, 488 nm, 496 nm, 502 nm, 514 nm); a He-Cd laser (325 nm, 442 nm); a continuously tunable laser in the frequency range 700-990 nm (Matisse Ti-sapphire laser), and another one in the range of 650-780 nm (Matisse Dye laser using Rhodamine 6G).

High-quality single mode lasers are highly desirable for Raman spectroscopy. However, laser sources with clean single frequencies are difficult to achieve due to the imperfections in laser optics and variations in laser gain medium, which result in stray light or sidebands in the unwanted frequency regime. Laser-line bandpass interference filters are traditionally used for filtering the laser sidebands, which are costly and designed for single frequencies. In our lab, gratings are adopted for the laser sideband filtering. Two different types of gratings are used-the volume Bragg gratings and regular ruled gratings.

The volume Bragg grating is a diffractive grating produced by refractive index modulation in the volume of a photosensitive material,¹⁴⁸ and the design and manufacture have been patented by OptiGrate Corp. A reflection volume Bragg grating consists of parallel plane grating surfaces of modulated refractive index fabricated on silicate glasses through holography and functions as a spectral filter as well as an angle filter, instead of the traditional ruled grating that disperses light. A narrow spectral range of the light beam

incident to the reflection volume Bragg grating is reflected within a narrow acceptance angle when the Bragg conditions are met, as shown in Figure 2-7a. Each volume Bragg grating is designed for a specific wavelength, where the spectral filtering can achieve less than 5 cm^{-1} to the laser line. In our experiments, volume Bragg gratings are used for 532 nm, 633 nm and 785 nm, for the ultralow frequency Raman spectroscopy measurements.

Figure 2-7 Schematics of laser sideband filtering through (a) a volume Bragg grating and (b) a ruled grating with a pinhole.

The sideband filtering for other laser frequencies employs a combination of a regular ruled grating and a pinhole, as shown in Figure 2-7b, where the green light represents the laser central frequency while the blue and orange lines stand for the sidebands. After being spatially dispersed from the laser central frequency through the ruled grating (1st order or high order), the sidebands are blocked by the pinhole and cannot enter the spectrometer. Since this technique is based on the spatial dispersion of light with different frequencies, a longer optical path from the ruled grating and the pinhole will result in a more effective filtering. In our experiments, a filtering limit of around 200 cm^{-1} to the laser line can be achieved in the visible range using the 1800 g/mm ruled gratings, given a distance of around 1 m from the grating to the pinhole. Although this filtering technique is not as effective as using the volume Bragg gratings, its main advantage lies in the low cost and adaptability for a wide frequency range.

Chapter 3 Sample Preparation and Characterizations

3.1 Mechanical Exfoliation of Transition Metal Dichalcogenide 2D Crystals

Transition metal dichalcogenide 2D crystals can be prepared through both top-down and bottom-up methods. The former often refers to the most widely employed mechanical exfoliation from bulk crystals through scotch tape, which was firstly introduced by Novosolov *et al.* and now has become a well-established method of preparing mono- and few-layer graphene sheets and many other 2D crystals.⁴⁴ This method is simple and most reliable for producing high crystalline quality samples. Another top-down method is exfoliation in liquids, involving techniques such as sonication, ion intercalation, and ion exchange, *etc.*^{45, 149} The liquid exfoliation method is good for scalable synthesis, while the exfoliated 2D crystals often come in very small planar sizes ($<1\ \mu\text{m}$). Most recently, researchers have successfully synthesized ultrathin and large-sized MX_2 2D crystals through vapor transport, a bottom-up method, where a careful control of the growth conditions is essential for obtaining good-quality samples.^{48, 150-152} In our experiments, the feasible mechanical exfoliation through scotch tape is adopted.

Single- and few-(TL) MoS_2 , MoSe_2 , WS_2 , and WSe_2 samples were exfoliated from bulk single crystal MoS_2 (SPI Supplies, Inc., USA), MoSe_2 (2D semiconductors Inc., USA), WS_2 (2D semiconductors Inc., USA) and WSe_2 (Nanoscience Instruments, Inc., USA) and then deposited onto the freshly cleaned Si substrates capped with a SiO_2 layer. Optical microscope (Olympus, EX51) was used to locate the single- and few-TL crystals. And atomic force microscopy (AFM, Dimension 3100, Veeco, USA) was used to confirm the TL number of the 2D crystals by measuring the film thicknesses in tapping mode in ambient conditions. Figure 3-1a shows the optical images of 1-10TL MoS_2 with lateral sizes of several microns on top of 90 nm SiO_2/Si substrates, where each thickness exhibits distinctive optical contrast (distinctive color in the optical image). The AFM images of 1-3TL MoS_2 are shown in Figure 3-1b, corresponding to the top left three optical images in Figure 3-1a. The height profiles are taken along the colored dashed lines in the AFM images, where 0.8 nm, 1.4 nm and 2.1 nm are corresponding to 1TL, 2TL and 3TL MoS_2 ,

respectively, consistent with the crystallography data and with previous reports¹⁵³⁻¹⁵⁵ (each TL corresponds to ~ 0.7 nm). Similarly, mono- and few-TL MoSe₂, WS₂, and WSe₂ also exhibit distinctive optical contrast on top of SiO₂/Si substrates, as shown by their optical images in Figure 3-2. Note that the exact colors that the 2D crystals appear in the optical images depend on the refractive indices of the materials, the thickness of the SiO₂ layer, the light source of the optical microscope, as well as the image processing of the software. Once the standard correspondence between the optical contrast (image color) and thickness is established through extensive AFM measurements, the TL number of a 2D crystal can be simply determined by its optical image, given that the substrates used are the same as the standard samples, and optical images are taken under the same conditions (same microscope, same light source, same light brightness, same image processing, *etc.*)

Figure 3-1 Optical and AFM images of exfoliated few-TL MoS₂ on 90 nm SiO₂/Si substrates. (a) Optical images of 1-10TL MoS₂. Each thickness shows distinctive optical contrast. The scale bars are 5 μm . (b) AFM images of 1-3TL MoS₂. (c) Height profiles taken along the green, red and blue dashed lines in (b) for 1TL, 2TL and 3TL MoS₂, respectively.

Figure 3-2 Optical images of exfoliated 1-7TL (a) MoSe₂ and (b) WS₂ on 100 nm SiO₂/Si substrates, and (c) WSe₂ on 90 nm SiO₂/Si substrates. The scale bars are 5 μ m.

3.2 Synthesis and Characterizations of Bismuth Chalcogenide 2D Crystals

High-quality Bi₂X₃ (X=Se, Te) 2D crystals with ultrathin thickness (down to 1QL), large planar size (micrometer scale or larger), and good crystalline quality are crucial for the research of their topological insulating as well as the thermoelectric properties, especially for the optical and electron transport measurements on single Bi₂X₃ thin film. The most well-established mechanical exfoliation method for preparing 2D crystals in graphene and transition metal chalcogenide systems, however, does not work as well in the bismuth chalcogenide systems, as shown in some scattered reports.¹⁵⁶⁻¹⁵⁸ Molecular beam epitaxial (MBE) is the most sophisticated method for Bi₂X₃ 2D crystal growth, where the layer-by-layer growth in atomic scale can be accurately controlled and monitored in time through the low-energy electron microscopy (LEEM).⁴⁶ However, MBE systems are very expensive and limited to a few research groups. Wet chemistry has also been demonstrated capable of synthesizing ultrathin Bi₂X₃ nanoplates, where however the planar size is still limited to a few hundred nanometers for 1QL and 2QL nanoplates.^{47, 159} Vapor transport is so far the most commonly used method for Bi₂X₃ 2D crystal growth since it is fast, cost-effective, contamination-free, and feasible to achieve a variety of Bi₂X₃ nanostructures.

Bi_2X_3 2D crystals down to few- and even single-QLs with micron scale planar sizes have been successfully grown on various substrates, like SiO_2/Si , mica, graphene, *etc.*¹⁶⁰⁻¹⁶² In our research, we adopted the vapor transport method to synthesize bismuth chalcogenide 2D crystals.

3.2.1 Vapor Transport Synthesis

Bi_2Te_3 2D crystals studied in this thesis were synthesized in a home-built vapor transport system, which is shown in Figure 3-3a. The synthesis chamber is a quartz tube with a length of 50 cm and a diameter of 2 inches, located within a single zone tube furnace (Lindberg Blue M, Thermo Scientific) whose temperature range can be varied from room temperature ($\sim 20^\circ\text{C}$) to 1100°C . The chamber is connected to several carrier gas supply lines, such as Ar, 5% H_2 in Ar, H_2 , N_2 and O_2 . The gas flow is controlled by a mass flow controller (MKS type 1479A) for each gas line and a four-channel readout (MKS type 247). The pressure of this vacuum system is controlled through a pressure controller (MKS type 250), a flow control valve (MKS 248A), a pressure gauge (MKS Baratron Capacitance Manometer), a thermocouple gauge (Kurt J. Lesker, KJL6000-VCR4) and the corresponding control and readout (Kurt J. Lesker, KJLC615), and a mechanical pump (Alcatel 2015SD, rotary vane pump). Note that the thermocouple gauge is for monitoring a pressure below than 200 mTorr. Most of the main parts of this vapor transport system are denoted with black arrows and labels in Figure 3-3a. Our home-built vapor transport system can achieve a base pressure of 5 mTorr and be operated in a wide range from base pressure up to 760 Torr. The controllable mass flow range is 4-200 sccm (standard cubic centimeter per minute) for Ar, 5% H_2 in Ar, N_2 , O_2 , and 10-500 sccm for H_2 , with an accuracy of 1 sccm.

Figure 3-3b shows the schematic of the vapor transport growth. The powder source is often located at the center of the tube furnace to achieve the best temperature control for the precursor, and the substrate is placed at the downstream of the precursor. The mechanism of the vapor transport growth is very straight forward: while being heated through the furnace, Bi_2Te_3 vapors come out from the powder source and are carried towards the downstream end with lower temperature by the carrier gas flow. Then the

Bi_2X_3 vapors will deposit on the substrates and recrystallize into Bi_2X_3 crystals. Temperature, pressure, carrier gas flow, and the location of the substrate are the controllable growth parameters and need to be carefully controlled. Note that the temperature drops sharply towards the end of the tube furnace (Figure 3-3b), indicating that the substrate experiences a large temperature distribution.

Figure 3-3 (a) Optical picture of the home-built vapor transport system. The main components are denoted by the black arrows and texts. (b) Schematic of the vapor transport growth within the synthesis chamber and the temperature profile of the tube furnace.

In our experiments, SiO_2/Si substrates used for the synthesis are cut into $1 \times 7 \text{ cm}^2$ strips, which are cleaned through sonication in acetone bath, then rinsed off by isopropanol and finally blow dried with N_2 gas. As cleaned SiO_2/Si substrates are then treated through oxygen plasma for 5 minutes under 150 W to remove any potential organic residue. During the synthesis, Bi_2Te_3 power (99.99%, Alfa Aesar) is positioned in the center of the quartz tube, and the as-prepared substrates placed around 15 cm downstream from the powder

source. Before the growth, the synthesis chamber was firstly evacuated to ~ 5 mTorr and then flushed several times with the carrier gas (Ar or H_2). We have tested a large variety of growth parameters and found that the best samples, in terms of ultrathin thicknesses and large planar sizes, can be obtained through growths conducted at 480°C under 100 Torr for 10 minutes, with a 30 sccm Ar or H_2 flow. The adoption of Ar or H_2 as carrier gas gives similar growth products.

Figure 3-4 Optical images of the as-grown Bi_2Te_3 nanoplates on SiO_2/Si substrates. (a) low-magnification bright field optical image taken through a 20X objective. (b) 50X-magnification bright field optical image. Nanoplates exhibit different colors. (c) Dark field optical image, showing the edge of the nanoplate as well as a bright dot in the center.

The optical images of the best as-grown Bi_2Te_3 nanoplates are shown in Figure 3-4, where the nanoplates typically come in hexagonal, triangular or truncated triangular shapes with a planar size of several microns. Different regions of the substrate gives different growth results due to the temperature distribution. The best samples often come in the central region (around $1 \times 1 \text{ cm}^2$) of the substrate chip. The higher temperature region normally results in thick nanoplates with large planar sizes up to tens of microns, and the nanoplate density is much lower than Figure 3-4a. The low temperature region gives thinner nanoplates while much smaller planar sizes ($1 \sim 2 \text{ }\mu\text{m}$) with a higher density. Figure 3-4b shows the bright field optical image of as-grown Bi_2Te_3 nanoplates with higher

magnification. The different colors exhibited by the nanoplates is an indication of different thicknesses, similar with the case of few-layer graphene and transition metal chalcogenide, as discussed above. A dim bright spot can be resolved in the centers of some nanoplates in the bright field optical images, which can be much better demonstrated by the dark field optical image, as shown in Figure 3-4c. These bright spots are related to the Te seeds that formed in the early stage of the growth, and will be discussed in detail in later sections.

Figure 3-5 (a) Bright field optical image of as-grown Bi_2Te_3 nanoplates on 100 nm SiO_2/Si substrates. (b) AFM images of 3QL, 4QL and 5QL nanoplates. The thickness profiles are taken along the corresponding colored dashed lines.

The thickness of the as-grown Bi_2Te_3 nanoplates are confirmed by AFM measurements. The thinnest nanoplate we can achieve is 3 nm thick, corresponding to 3QL (Note that the thickness of 1QL is around 1 nm, as discussed in section 1.2.2). Figure 3-5b shows the AFM images of three nanoplates with a thicknesses of 3 nm, 4 nm, and 5 nm, respectively, whose height profiles are taken along the colored dashed lines and plotted in the corresponding colors on the right panel. A small, thicker part can be clearly seen in the AFM images of the 3QL and 4QL nanoplates (Figure 3-5b, left and middle images), respectively, being 1 nm and 3 nm thicker than the rest flat parts of the nanoplates. The irregular film-shaped 1 nm feature in the 3nm nanoplate is suspected be the fourth QL at an intermediate stage forming on top of the nanoplate underneath, indicating a layer-by-

layer growth process. Extensive AFM measurements confirm that different colors of the nanoplates represent different thicknesses and there is a one-to-one projection in between.

Figure 3-5a shows the bright field optical images of 3-9QL and even thicker Bi_2Te_3 nanoplates. The optical contrasts for nanoplates thinner than 9QL are very distinct for each thickness and can be easily distinguished by the optical images. Nanoplates above 9QL appear to be brighter than the thinner ones and not as distinguishable. The excellent optical contrasts for few-QL Bi_2Te_3 provides a quick and convenient approach for the nanoplate location and thickness identification under optical microscope, which is highly favorable for further optical characterizations and electronic device fabrications.

Figure 3-6 Optical and AFM images of vapor transport grown Bi_2Te_3 and Bi_2Se_3 2D crystals on mica substrates. (a) Bright field optical images of 2-4QL Bi_2Te_3 . (b) Bright field optical images of 1-5QL Bi_2Se_3 nanoplates. (c-e) AFM images of 2QL Bi_2Te_3 and 1-2QL Bi_2Se_3 nanoplates. The inset thickness profiles are taken along the red dashed lines.

Using the same vapor transport method, both Bi_2Te_3 and Bi_2Se_3 2D crystals have been successfully grown on mica substrates by our collaborators J. Wu and H. Peng *et al.*^{49, 162} Figure 3-6a and b display the optical images of as-grown 2-4QL Bi_2Te_3 nanoplates, and 1-5QL Bi_2Se_3 nanoplates on mica substrates with a planar size of a few microns, respectively. The few-QL Bi_2X_3 nanoplates do not exhibit different colors in this case but different brightness of the same shade. The thicknesses of the Bi_2X_3 nanoplates were accurately determined by AFM measurements, as shown in Figure 3-6c, d and e, where a thickness of

~ 1.5 nm was assigned to 1QL Bi₂X₃ and ~2.5 nm to 2QL. A slightly larger measured thickness than the predicted value (~ 1 nm for 1QL and ~2 nm for 2QL) is probably due to some adsorbates such as water molecules on the surface of the nanoplates, in addition to a surface lattice relaxation effect, where both the inter-QL and intra-QL lattice constants at the surface are expected to increase by a few percent than in the bulk.^{163, 164} Moreover, other factors such as the force constant difference between the substrates and the nanoplates in the AFM measurements, as well as the substrate-dependent interface spacing,¹⁶³ might also contribute to the abovementioned discrepancies in the QL number determination based on AFM measured thicknesses.

3.2.2 Optical Contrast of Few-Quintuple Bi₂Te₃ on SiO₂/Si Substrates

Bi₂X₃ 2D crystals are perfectly visible through optical microscopy, as shown in the previous section. The colors exhibited by Bi₂Te₃ 2D crystals on the SiO₂/Si substrates can be quantitatively understood in terms of optical contrast, similar with the case of graphene and transition metal chalcogenide 2D crystals. Optical contrast in the three-layer thin film system (Bi₂Te₃/SiO₂/Si) originates from the interference of the reflected light from different interfaces. The presence of the opaque Bi₂Te₃ thin film adds an optical path, changing its interference color respect to the empty SiO₂/Si substrates.¹⁶⁵ The optical contrast here is defined as the Michelson contrast¹⁶⁶

$$\text{optical contrast} = \frac{R_{\text{Bi}_2\text{Te}_3} - R_{\text{SiO}_2}}{R_{\text{Bi}_2\text{Te}_3} + R_{\text{SiO}_2}}, \quad (3-1)$$

where $R_{\text{Bi}_2\text{Te}_3}$ is the reflected light from the Bi₂Te₃ nanoplate and R_{SiO_2} is that from the bare SiO₂/Si substrates, as shown by the dashed lines in Figure 3-7a. The value of optical contrast ranges from -1 to 1 and the positive (negative) sign indicates a stronger (weaker) reflection from the Bi₂Te₃ nanoplate than from the substrates. To quantitatively characterize the optical contrast of few-QL Bi₂Te₃ on SiO₂/Si substrates, reflectivity was measured from the as-grown nanoplates via a micro-reflection spectrometer (Craic 20) using a 5 μm sized aperture. Figure 3-7b displays the measured optical contrast spectra in the visible region (400~750 nm) for few-QL and bulk Bi₂Te₃ nanoplates. A contrast minimum can be seen in the spectra for 3-8QL, exhibiting a blueshift while increasing the

thickness, as denoted by the black arrow. For even thicker nanoplates (12QL and above), the contrast minimum cannot be identified, which has probably shifted out of the visible region following the blue-shifting trend. The 3QL and 4QL nanoplates show negative optical contrast through the whole visible region, which is consistent with the fact that they appear darker than the substrates in the optical images. From 5QL, positive contrast starts to show up in the red region of the spectrum. The positive contrast becomes more and more dominant with increased thickness and covers the whole visible range in the limit of bulk, explaining why thicker nanoplates appear brighter to eyes under the optical microscope.

Figure 3-7 (a) Schematic of the optical reflection and transmission with normal incidence in the Bi₂Te₃/SiO₂/Si system. Solid lines indicate the incident light and dashed lines stand for the reflected light. (b) Measured optical contrast spectra of as grown few-QL Bi₂Te₃ nanoplates on 100 nm SiO₂/Si substrates. (c) Calculated optical contrast of Bi₂Te₃ thin films with thicknesses from 1 QL to bulk on 100 nm SiO₂/Si substrates.

To explain the observed optical contrast in our Bi₂Te₃/SiO₂/Si system, calculations through MATLAB were carried out based on the Fresnel's equations, where a simple normal incidence geometry^{165, 167} was used, as shown in Figure 3-7a. The refractive indices of the four different media (air, Bi₂Te₃, SiO₂, and Si) required for the optical contrast calculations are obtained from existing literatures.¹⁶⁸⁻¹⁷⁰ The calculated optical contrasts for 1-200QL Bi₂Te₃ on 100 nm SiO₂/Si substrates are shown in Figure 3-7c, where the contrast spectra for 1QL and 2QL are in dashed lines, and those for 3QL and above are in solid lines. The optical contrasts for 50QL and above are identical, indicating that the 50QL Bi₂Te₃ is completely opaque over the visible range and should appear the same as the bulk crystal. The calculated results show a blueshift of the contrast minimum as the thickness

of Bi_2Te_3 increases, qualitatively in consistent with the experiments. Quantitatively, the experimental and calculated results match well in the case of bulk Bi_2Te_3 but not for few-QL nanoplates. This discrepancy indicates that the refractive index of few-QL Bi_2Te_3 might be different from that of their bulk counterpart, given that the refractive index of bulk Bi_2Te_3 was used in the calculations for all thicknesses. Another factor that could contribute to the discrepancy is the simplified normal incidence model employed for the contrast calculations, while for the experiments an objective with numerical aperture of 0.5 was used. C. Casiraghi *et al.* reported that the objective numerical aperture could affect both the shape and intensity of the contrast spectrum.¹⁷¹ A more complex model¹⁶⁶ considering the incident light angle and profile might be able to characterize our system better but it is beyond the scope of this thesis.

Figure 3-8 Two-dimensional plot of the calculated optical contrast for $N\text{QL Bi}_2\text{Te}_3$ ($N=1-10$) on the SiO_2/Si substrates within the visible range (400~800 nm) as a function of the oxide layer.

The thickness of the SiO_2 layer is essentially important to determine the optical contrast in the $\text{Bi}_2\text{Te}_3/\text{SiO}_2/\text{Si}$ system. To optimize the substrate conditions for the visibility of Bi_2Te_3 2D crystals, calculations with different thicknesses of the oxide layer were conducted. Figure 3-8 shows the 2D plot of the calculated optical contrast spectra for 1-10QL Bi_2Te_3 with varying SiO_2 thickness from 0 nm to 600 nm. The color bar on the right of the plot denotes the values of the optical contrast at each data point. The calculated

results show that 100 nm of the SiO₂ layer can result in the highest contrast under visible illumination for few-QL Bi₂Te₃, similar with previous reports on few-QL Bi₂Se₃ nanoplates.¹²⁸ And this is exactly the reason why we adopted the 100 nm SiO₂/Si as the substrates for the growth of Bi₂Te₃ 2D crystals.

3.2.3 Te-Seeded Epitaxial Growth of Bi₂Te₃ Nanoplates

Despite of a large number of reports on the vapor transport growth of Bi₂X₃ 2D crystals, there still lacks a comprehensive investigation on the growth mechanism, which however, is essentially important in terms of controllable synthesis, structural design and functional engineering. In this thesis, we present a Te-seeded growth mechanism of Bi₂Te₃ nanoplates through careful characterizations and analyses.

Figure 3-9 (a) Low-magnification SEM image of as-grown Bi₂Te₃ nanoplate. (b) High-magnification image of a triangular nanoplate with a spot-like feature in the center of the nanoplate which is highlighted by the red circle. (c) Corresponding optical image of the nanoplate in (b). (d) Zoom-in image of the spot-like feature in (b), showing a growing top layer. (e) High-magnification image of a hexagonal nanoplate with a spot-like feature in the center of the nanoplate which is highlighted by the red circle. (f) Corresponding optical image of the nanoplate in (e). (g) Zoom-in image of the spot-like feature in (e), showing a growing top layer and the nucleation center.

An interesting bright spot has been observed in the center of some as-grown Bi₂Te₃ nanoplates, as shown by the optical images in section 3.2.1. A further characterization of

the morphology of the central bright spots are conducted through scanning electron microscopy (SEM). Figure 3-9a shows the low-magnification SEM image of the as-grown Bi_2Te_3 nanoplates on SiO_2/Si substrates. The central bright spots can be resolved in both SEM and optical images, as denoted by the red circles in Figure 3-9b, c, e, and f. High-magnification SEM images (Figure 3-9d and g) indicate that these spot-like features possess a particle or thin film morphology. The thin films likely correspond to a growing top layer, implying a layer-by-layer growth. The top growing layer seems to be originated from the central particle, which indicates that the bright spot might function as the nucleation seed.

Figure 3-10 HAADF images of two hexagonal Bi_2Te_3 nanoplates on holey carbon. The image contrast is proportional to the plate thickness. (a) shows a thicker nanoplate with holes in the center, where the seed was located. (b) shows a thinner nanoplate. The nanoplates crystallize in the Tellurobismuthite $R\bar{3}m$ phase. The facets of the hexagons are $\{03\bar{3}0\}$ planes, as observed from the SAED pattern in (c). The growth direction perpendicular to the substrate is the $[0001]$.

Transmission electron microscopy (TEM) is adopted to further characterize the crystalline structure and the composition of the particle-like feature in the center of as-grown Bi_2Te_3 nanoplates. The nanoplates are released from the substrates through a polymethyl methacrylate (PMMA) transfer technique instead of the conventional “sonication and dispersion” method to avoid the morphology damage of the nanoplates, especially the large-sized ones. SiO_2/Si substrates with as-grown Bi_2Te_3 nanoplates on top was firstly spin coated on a layer of PMMA with the thickness of ~ 300 nm. After being

baked for 5 min at 180°C, the PMMA coated substrate was immersed in buffered HF solution for a few hours. The 100 nm SiO₂ layer would be etched away according to the chemical reaction $SiO_2 + 4HF \rightarrow SiF_4(g) + 2H_2O$ and thus the PMMA film with Bi₂Te₃ nanoplates embedded in was released from the Si substrates. The PMMA film was then rinsed off using deionized water and transferred to TEM grids covered with lacey carbon. PMMA was then removed by acetone, leaving Bi₂Te₃ nanoplates on the lacey carbon.

Figure 3-10 shows the released Bi₂Te₃ samples on lacey carbon studied under aberration corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) conditions (Titan STEM). Figure 3-10a and b show two different hexagonal nanoplates where the image contrast is proportional to the nanoplate thickness (the brighter hexagon (a) is thicker while the darker (b) is thinner). We found that the nanoplates crystallize in the Tellurobismuthite $R\bar{3}m$ phase. The facets of the hexagons are $\{03\bar{3}0\}$ planes, as observed from the selected-area electron diffraction (SAED) pattern (Figure 3-10c). The growth direction is identified to be along the [0001] axis perpendicular to the hexagon plane from the SAED pattern. It is worth to note that small holes were found in the center of the nanoplate and notches on the edge. The notches on the edge were probably caused by the accidental damage during the transfer process. Cheng *et al.* have reported similar center-hollowed Bi₂Te₃ nanoplates broken from T-shaped Bi₂Te₃ (nanoplate)-Te (nanorode) heterojunctions.¹⁷² In our as-prepared TEM samples, the holed features were commonly present in the released Bi₂Te₃ nanoplates and we tentatively propose that they might be related to the nucleation seeds (bright spots in Figure 3-4c), which are left over during the releasing process, causing the holed features in the released nanoplates.

To further characterize the possible nucleation seeds in the center of the Bi₂Te₃ nanoplates, planar-view and cross-section TEM samples were prepared from the as-grown Bi₂Te₃ nanoplates on SiO₂/Si substrates. The planar samples were prepared by thinning the backside of the substrates using conventional electron microscopy sample preparation methods (mechanical polishing). For the cross-section samples, two pieces of substrates with nanoplates on top were glued together with the face-to-face. Then, conventional polishing was laterally performed up to get a sample with a thickness of around 20 μm,

which was then attached to a copper grid. Finally, precision ion polishing was carried out in a Precision Ion Polishing System (PIPS) to obtain an electron transparent sample.

Figure 3-11 Planar view of Bi_2Te_3 nanoplates on SiO_2/Si substrates. (a) HAADF of the studied nanoplate. (b) Surface plot of the plate in (a). (c) Low magnification HAADF image of the studied area. (d) Intensity profile taken from the black square in (a) along the arrow indicated direction. (e) HRTEM image of the darker feature in the black squared region in (a). (f) FFT of image (e).

Figure 3-11a shows the HAADF image of a typical Bi_2Te_3 nanoplate with truncated triangular morphology from the studied area (Figure 3-11c) and its surface plot is presented in Figure 3-11b. A darker contrast (denoted by the black square in figure part a) was revealed in the nanoplate, and is clearly shown in the intensity profile (Figure 3-11d) performed along the direction indicated by black arrow. The contrast difference can be due to a thickness change or to a compositional variation. The HRTEM analysis of this darker contrast region shows a particle-like agglomerate with a size of around 50 nm, as shown in Figure 3-11e. Through the study of the fast Fourier transform (FFT) (Figure 3-11f) of the image e, we can identify not only the Bi_2Te_3 and the Si phases, but also the hexagonal tellurium phase (space group $P3_121$), as shown in the indexed FFT (Figure 3-11g). The identification of the Te phase can explain the darker contrast of this region in a HAADF image, since the image intensity is proportional to the squared atomic number ($Z_{\text{Bi}}^2 = 6889$;

$Z^2_{\text{Te}} = 2704$). Moreover, the Te phase shows a $(11\bar{2}0)[0001]\text{Te} // (11\bar{2}0)[0001]$ epitaxial relationship with the Bi_2Te_3 phase, as denoted in Figure 3-11g. Notice that the green hexagon in Figure 3-11f represents the $\{1\bar{2}10\}$ lattice planes of both the Bi_2Te_3 and Te phases while the yellow hexagon only represents the $\{10\bar{1}0\}$ planes of Te. The epitaxial relationship can be further identified as perfect epitaxy along the c axis since the in-plane lattice mismatch is only 1.6% for the Te ($a=4.447 \text{ \AA}$) and Bi_2Te_3 ($a=4.375 \text{ \AA}$) phases.¹⁷³ The crystalline Te phase and the Te/ Bi_2Te_3 epitaxy have also been identified in several other Bi_2Te_3 nanoplates in the studied area (Figure 3-11c).

The appearance of the Te phase in the Bi_2Te_3 nanoplates can be understood from analyzing the detailed vapor transport growth process- Bi_2Te_3 sublimation and recrystallization. Early measurements on the vapor pressure of crystalline Bi_2Te_3 indicated that the sublimation occurred congruently below the melting temperature 585°C , following the decomposition reaction $\text{Bi}_2\text{Te}_3(s) \rightarrow 2\text{BiTe}(g) + 1/2\text{Te}_2(g)$,¹⁷⁴⁻¹⁷⁶ while later Brebrick *et al.* casted doubt on the validity of the proposed reaction for an equilibrium sublimation and suggested an incongruent sublimation process with Te-rich (atomic percent $> 60\%$) vapor species.¹⁷⁷ During the vapor transport growth, BiTe and Te_2 molecules (major vapor species) sublimating from the Bi_2Te_3 powder source are carried with the gas flow to a lower temperature zone and deposit on the substrates into Bi_2Te_3 nanoplates, according to the synthesis reaction $2\text{BiTe}(g) + 1/2\text{Te}_2(g) \rightarrow \text{Bi}_2\text{Te}_3(s)$. The wide presence of the Te crystalline seeds in as-grown Bi_2Te_3 nanoplates implies an excess of the Te_2 molecules in the sublimated vapor species, in agreement with the report from Brebrick *et al.*¹⁷⁷ A Te-rich composition will lead to a phase segregation during the crystallization process and thus the formation of two equilibrium crystalline phases, Bi_2Te_3 and Te, according to the Bi-Te binary phase diagram.¹⁷⁸ The identification of the Te/ Bi_2Te_3 epitaxial relationship as elucidated by transmission electron microscopy, suggests a Te-seeded epitaxial growth of Bi_2Te_3 nanoplates in our vapor transport process.

Figure 3-12 STEM cross-section analysis of an as-grown Bi_2Te_3 nanoplate on SiO_2/Si substrates. (a) HAADF image of the nanoplate studied, displayed also as surface plot below. The colored frames indicate the regions where the atomic resolution HAADF STEM analyses were performed. (b) Mapping of the EELS Te signal (cyan colored) and Bi signal (pink colored). (c) Bottom interface between the Bi_2Te_3 nanoplate and SiO_2/Si substrates taken in the region pink squared in (a), showing a few pure Te layers in between. One QL of Bi_2Te_3 is denoted by the white dashed lines. (d) Interface between the Bi_2Te_3 nanoplate and the attached Te structure on the lateral side, taken in the blue squared region in (a). (e) Atomic resolution HAADF STEM image of the Bi_2Te_3 structure, taken in the region orange squared in (a). The inset corresponds to the simulated structure by using the STEM-CELL software.¹⁷⁹ (f) FFT of (e). (g) FFT of the Te aggregation, green squared in (d). (h) FFT of (d), showing the epitaxy between the Bi_2Te_3 and the Te aggregation.

The proposed epitaxial growth mechanism is further analysed on cross-section samples under HAADF STEM conditions by using an aberration-corrected microscope. Figure 3-12a shows a HAADF STEM image of a nanoplate with thickness of around 300 nm, along with its surface plot below to show the nanoplate morphology. Electron energy loss spectroscopy (EELS) analysis was performed to study the elemental constitution of the nanoplate and the mapping results are presented as Figure 3-12b. The bright cyan color on the right side of the nanoplate corresponds to a pure Te structure aggregated at the lateral facet of the plate. Furthermore, it was found that the Te phase exists in the pinholes in the SiO_2 layer until it reaches the Si substrate, while the Bi signal is restricted only to the

nanoplate. Figure 3-12c (pink squared region in Figure 3-12a) shows the atomic resolution HAADF STEM image of the interface between the Bi₂Te₃ nanoplate and the SiO₂ layer of the substrates, where five atomic layers Te-Bi-Te-Bi-Te can be identified as a QL (the Bi and Te atoms are highlighted as pink and cyan dots, respectively). Between the bottom QL of the Bi₂Te₃ nanoplate and the SiO₂/Si substrates, three atomic layers of Te can be seen. Again, the perfect epitaxial relationship can be directly identified between the Te atomic layers and the bottom QLs of the Bi₂Te₃ nanoplate along the *c* axis. The Te crystalline layer at the interface is only present in the pinholed region and should be closely related to the Te nucleation seed as discussed above. We tentatively propose that most of the Te nucleation happens at the pinhole pits, since thermodynamically the substrate imperfections could facilitate the heterogeneous nucleation by vapor condensation.¹⁸⁰ The pinholed feature embedded in the SiO₂ layer may result in an attachment between the nucleation seed and the Si substrates. During the nanoplate releasing process through HF etching, the SiO₂ layer gets etched away following the reaction $SiO_2 + 4HF \rightarrow SiF_4(g) + 2H_2O$, while the Te pinhole remains. The Te seed might be tore off the rest of the nanoplate due to its attachment to the Si substrate, thus leaving a holed feature in some released Bi₂Te₃ nanoplates (Figure 3-12a).

Figure 3-12d (blue squared region in Figure 3-12a) displays the atomic resolution interface between the Bi₂Te₃ nanoplate and the laterally attached Te structure, where an imperfect epitaxial relationship can be observed with the presence of some misfit dislocations at the interface. This epitaxial relationship can be further studied from the FFT analysis of the blue and green squared regions as (0001)[$\bar{1}2\bar{1}0$] Bi₂Te₃ // (0001)[$\bar{1}2\bar{1}0$] Te (see Figure 3-12g & h), with a slight angle between the (0001) planes of the two phases. The lattice mismatch along the *c* axis between the Te and Bi₂Te₃ phases is around 2.7% (*c*=30.39 Å for Bi₂Te₃; *c*=5.92 Å for Te),¹⁷³ and a perfect in-plane epitaxy is expected for such a small mismatch, as the case out of plane. The observed imperfect in-plane epitaxy can be explained by the inhomogeneity of Bi₂Te₃ along the *c* axis. The atomic layers are evenly spaced along the *c* axis in Te but not in Bi₂Te₃ due to the presence of the vdW gaps. In fact, 2.7% is underestimating the lattice mismatch assuming an even atomic-layer spacing along the *c* axis for both Bi₂Te₃ and Te, and the misfit dislocations observed at the

interface can be attributed to a real lattice mismatch that is much bigger. After a few nanometers from the interface, the Te phase relaxes from the strain caused by the interface and aligns perfectly in plane with the Bi_2Te_3 phase. Thus far, an epitaxial relationship between the six-fold symmetry Te ($P3_121$) and Bi_2Te_3 ($R\bar{3}m$) phases has been confirmed both along and perpendicular to the c axis. It is worth to note that two different Bi_2Te_3 crystalline orientations were observed in the orange squared region (Figure 3-12e) and the blue squared region (Figure 3-12d), indicating the presence of a twin boundary somewhere in between. In polycrystalline Bi_2Te_3 , (0001) basal twin boundaries have been observed with a termination at the vdW gaps between two adjacent QLs.^{181, 182} This twin boundary configuration has also been confirmed to be energetically favorable, according to the *ab initio* calculations.¹⁸¹ Therefore, we believe that the same (0001) basal twin boundary also presents in the nanoplate studied here. Considering the fact that the crystalline orientation keeps the same in a range of tens of QLs (between the orange and pink regions), we assume that twin boundaries are unlikely to present in the case of few-QL nanoplates.

The nanoplate studied in Figure 3-12 well represents some percentage of as-grown nanoplates where the central Te nucleation seeds cannot be identified from the top-view optical and STEM images. Note that during the vapor transport growth, the volume of both Bi_2Te_3 and Te crystalline phases will gradually increase with a continuous Te-rich vapor supply and condensation, as a result of the Bi_2Te_3 -Te phase segregation, as discussed above. In the condition of fast Bi_2Te_3 phase formation, the central Te seed might get merged in the Bi_2Te_3 nanoplate. Consequently, the growth of the nucleation seed will be cut off with a lack of Te supply. Instead, the excess Te adatoms will crystallize into a new Te crystalline phase on the surface of the nanoplate, corresponding to the Te aggregation shown in Figure 3-12b. We tentatively believe that extra Te aggregation is most likely to present on large and thick nanoplates, where the nanoplate growth is more rapid and larger quantity of Te phase is expected, in comparison with the few-QL cases.

Thus far, combining all the above characterizations (optical microscopy, AFM, SEM, aberration corrected HAADF STEM), we propose a nanoplate growth model: during the early growth stages, the Te-rich vapor species sublimated from Bi_2Te_3 powder source condensate on the substrates (preferably at the pinhole locations), forming Te crystalline

seeds. During the condensation process, some vapors are inclined to diffuse through the SiO₂ pinholes and then solidify, resulting in an attachment between the nucleation seeds and the Si substrates. Meanwhile, the BiTe and Te₂ vapors will get adsorbed to the Te nucleation seeds and react into Bi₂Te₃, growing epitaxially into nanoplates. The epitaxial growth occurs both laterally and vertically, following a layer-by-layer manner. The thickness of the nanoplate is determined by the size of the nucleation seed as well as the supply of BiTe and Te₂ vapors. The absence of the nucleation seeds in some nanoplates likely suggest that the Te seeds either get merged into the Bi₂Te₃ nanoplates due to the fast growth process, or react with BiTe vapors and are completely converted to Bi₂Te₃.

3.2.4 Electron Transport Properties of Ultrathin Bi₂Te₃ Nanoplates

The electronic and spintronic applications of the 3D topological insulators rely on the electron transport properties of the novel surface states. Even though the conducting surface state can be easily probed through ARPES, its detection through electron transport is still challenging. The main reason is that those small-gapped topological insulator materials (Bi₂Se₃, Bi₂Te₃, Sb₂Te₃) are naturally heavily doped and the surface carriers are often overwhelmed by the bulk carriers during electron transport measurements. There mainly exist three routes that are widely adopted by researchers to enhance the contribution of the surface states during transport: (1) studying low-dimensional topological insulators for their large surface-to-volume ratios; (2) decreasing the bulk carrier concentration through elemental compensation doping; (3) reducing the bulk carrier concentration through electric gating. Generally, two or even three of the routes need to be simultaneously employed to achieve an effective tuning of the bulk carrier density. The surface state contribution will be largely enhanced when the Fermi level is tuned into the bulk band gap, as has been demonstrated by the ambipolar gate effect in binary or ternary topological insulator FET devices.^{111, 112, 183-185} In this thesis, we investigate the electron transport properties of vapor transport grown Bi₂Te₃ nanoplates through electrical gating.

Figure 3-13 Schematic flow chart of the device fabrication process through electron beam lithography.

FET devices were fabricated on the as-grown Bi_2Te_3 nanoplates by the standard electron beam lithography (EBL), metal deposition and lift-off process, whose schematic flow chart is shown in Figure 3-13. Two type of positive e-beam resists, methyl methacrylate 8.5 (MMA 8.5, Micro Chem) and polymethyl methacrylate (PMMA 4, Micro Chem), are used for the EBL process. A layer of MMA is firstly spin coated (Specialty coating systems, INC. Spincoater model P6700) on the SiO_2/Si substrates with as-grown Bi_2Te_3 nanoplates on top at a speed of 4000 rounds per minute for one minute. The substrate coated with the MMA layer is then baked on a hot plate under 180°C for 5 min, after which a layer of PMMA is spin coated on top with the same recipe (4000 rounds per min, one minute) and then baked under 180°C for 5 min. The thickness of the MMA/PMMA bilayer is around 200/300 nm. The lithography process is then conducted on the as-prepared substrates within a JEOL 7001F field emission SEM equipped with a beam blanker (Deben) and nanometer pattern generation system (NPGS). Pre-designed patterns through DesignCAD are lithographed on the MMA/PMMA bilayer, where the parts that have been exposed to the electron beam can be dissolved in a developer solution, while the unexposed parts remain. The exposed MMA layer dissolves faster than the top PMMA layer then therefore forms an under-cut structure, which will benefit the later lift-off process. The developer solution is a mixture of methyl isobutyl ketone (MIBK) (99.5%, Sigma) and isopropanol

alcohol (IPA) (99.7%, Sigma) with a ratio of 1:3 and the developing process in our experiments lasts around 1 min followed by a rinse-off through IPA and blow-dry by N₂ gas. The step after the development is metal deposition in a thermal evaporator (Elite Engineers), where Cr/Au (5 nm/100 nm) is used for our Bi₂Te₃ nanoplate devices with Ohmic contacts. The last step of the device fabrication process is to lift-off the rest MMA/PMMA resist in acetone, after which the designed patterns covered with metal are left on the substrates.

Following the process described above, FET devices with a Hall bar geometry are fabricated on as-grown Bi₂Te₃ nanoplates with different thicknesses. Figure 3-14 shows the schematic of a six-terminal Hall-bar structure adopted (a) and the corresponding optical image of a FET Hall device fabricated on a 4QL Bi₂Te₃ nanoplate (b). The light grey area in Figure 3-14a represents the sample with a regular bridge shape and the dark grey area stands for electrode pads. A constant current I is driven through the sample between the source (S) and drain (D). The voltage drop along and perpendicular to the current flow can be measured through the rest four probes as V_{xx} and V_{xy} , respectively. Consequently, the longitudinal (R_{xx}) and transverse (R_{xy}) resistance are defined as follows: $R_{xx} = V_{xx}/I$ and $R_{xy} = V_{xy}/I$. Note that R_{xx} measures the resistance of the sample through a four-probe configuration and R_{xy} stands for the Hall resistance with the presence of a magnetic field B perpendicular to the sample plane. For a 2D thin film, R_{xy} and B often hold a linear relationship $R_{xy} = -\frac{B}{n_s e}$, where the sheet carrier concentration n_s of the sample can be estimated through the slope $R_H = -\frac{1}{n_s e}$, which is referred to as the Hall coefficient. The conductivity elements of the 2D film within a magnetic field are defined as

$$\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2}, \sigma_{xy} = \frac{\rho_{xy}}{\rho_{xx}^2 + \rho_{xy}^2}, \quad (3-2)$$

where $\rho_{xx} = R_{xx} \frac{W}{L}$ with W and L being the width and length of the channel, respectively, and $\rho_{xy} = R_{xy}$.¹⁸⁶

Figure 3-14 (a) Schematic of a six-terminal Hall-bar structure. (b) Optical image of a Hall device fabricated on an as-grown 4QL Bi_2Te_3 nanoplate on top of SiO_2/Si substrate.

Hall measurements are very sensitive to the geometry of the actual device. Ideally, the sample are required to have a regular bridge shape as shown in Figure 3-14a, to restrict the longitudinal current flow. Patterning and etching are often involved to achieve the standard Hall-bar structures, as commonly used for fabricating the graphene Hall devices.^{187, 188} In our experiments, the six-probe Hall bars are fabricated directly onto the as-grown hexagonal or triangular Bi_2Te_3 nanoplates as shown in Figure 3-14b, due to the experimental difficulty of patterning and device fabrication on the scale of several microns. The width of six probes contacting the nanoplate is around 600 nm, and the distance between the source and drain probes is around 6 μm . The Hall resistance is generally underestimated in our experiments due to the protruding Hall bars, and the driven current flow might not be strictly along the source and drain direction. However, useful information can still be obtained in spite of some systematic error caused by the irregular geometry of the Hall device.

Low-temperature electron transport measurements were conducted in a Physical Property Measurement System (PPMS, Quantum Design), where the lowest temperature achievable is 2.5 K and the magnetic field can go up to 9 T. The sample holder can be rotated within $\pm 90^\circ$, to achieve different angles between the Bi_2Te_3 nanoplate and the magnetic field. The constant current is provided by a lock-in amplifier (Stanford Scientific SR520) and the voltage signals V_{xx} and V_{xy} are collected through two lock-in amplifiers (Stanford Scientific SR520) that are synchronized at 13 Hz. For the gate response

investigation, a DC gate voltage is applied to the back side of the SiO₂/Si substrates and the SiO₂ functions as the dielectric layer. The breakdown voltage of the 100 nm SiO₂ layer is between 80 and 100 V. Laboratory Virtual Instrumentation Engineering Workbench (LabVIEW) was used to program the measurement control and data acquisition system.

Figure 3-15 (a) Temperature-dependent resistance of 4QL, 7QL, and 11 QL Bi₂Te₃ nanoplates. (b) Magnetoconductivity of 4QL Bi₂Te₃ with the magnetic field parallel and perpendicular to the nanoplate, respectively. (c-d) Temperature dependence of (c) the magnetoconductivity and (d) the phase coherence length of 4QL Bi₂Te₃.

The measured temperature-dependent longitudinal resistance (R_{xx}) of 4QL, 7QL and 11QL Bi₂Te₃ nanoplates are shown in Figure 3-15a. Overall, the resistance decreases with increasing thickness, consistent with the results of the MBE grown topological insulator thin films.^{189, 190} In a higher temperature range (10 K to 300 K) where phonon scattering dominates, the resistance decreases with decreasing temperature, showing a metallic behavior. The resistance reaches a minimum at 10 K and shows an upturn when the temperature further goes down to 2 K, which is primarily attributed to the carrier freeze-

out effect, similar to the previous report on Bi₂Te₃ nanoribbon.¹⁰⁹ The magnetoresistance is measured with magnetic field up to 9 T and weak anti-localization (WAL) effect was observed in the small magnetic field range (< 0.5 T). Figure 3-15b plots the quantum interference correction to the magnetoconductivity, defined as $\Delta\sigma(B) = \sigma(B) - \sigma(0)$, of the 4QL nanoplate measured at 2.5 K. The WAL effect appears as a sharp magnetoconductivity peak at B=0 T with the presence of a magnetic field perpendicular to the nanoplate, as shown by the blue curve. When the magnetic field is parallel to the nanoplate, the magnetoconductivity is much suppressed, as a result of the ultrathin thickness of the nanoplate.¹⁹¹ Similar WAL effect has also been observed in thicker nanoplates.

The WAL effect originates from the strong spin-orbit coupling in Bi₂Te₃ and the conductivity correction $\Delta\sigma$ can be well described by the Hikami-Larkin-Nagaoka (HLN) formular¹⁹²

$$\Delta\sigma(B) = \alpha \frac{e^2}{\pi\hbar} \left[\Psi\left(\frac{1}{2} + \frac{\hbar}{4eBl_\phi^2}\right) - \ln\left(\frac{\hbar}{4eBl_\phi^2}\right) \right], \quad (3-3)$$

where e is the electronic charge, $\hbar$ is the Planck's constant, l_ϕ is the phase coherence length, and $\psi(x)$ is the digamma function with the formula

$$\psi(x) = \ln(x) - \frac{1}{2x} - \frac{1}{12x^2} + \frac{1}{120x^4} + O\left(\frac{1}{x^6}\right). \quad (3-4)$$

The high-order terms $O(\frac{1}{x^6})$ of the digamma function can normally be neglected.

Theoretically, the prefactor α should be equal to 1, 0, and -0.5, corresponding to the weak spin-orbit coupling and magnetic scattering, strong magnetic scattering, and the strong spin-orbit coupling cases. For topological insulators with strong spin-orbit coupling effect, a value of -0.5 is expected for α , and has been experimentally confirmed in Bi₂Se₃.^{110, 185} The temperature dependence of the WAL effect has been investigated on the 4QL device at four different temperatures (2.5 K, 10 K, 20 K and 40 K), as shown in Figure 3-15c. As the temperature increases, the WAL peak becomes broadened and weakened, and finally disappears, due to the decrease of the phase coherence length at higher temperature. The

HLN formula is applicable only within small magnetic field ($B_c \sim \frac{h}{el_\phi^2}$)¹⁹³ and here we fit the magnetoconductivity curves at different temperatures within the range of 0.2 T using α and l_ϕ as fitting parameters. Figure 3-15d displays l_ϕ vs. T under logarithmic scale. The phase coherence length decreases with increasing temperature following a $l_\phi \sim T^{-1/2}$ relationship as guided by the fitted red line, in consistent with the theoretical prediction for the 2D system.^{194, 195}

The gate response of the WAL effect is investigated on nanoplates with different thicknesses at 2.5K with the magnetic field perpendicular to the nanoplates. The back gate tuning range is from 40 V to -100 V with a step of 20 V. Figure 3-16 a-c show the gate-dependent of the magnetoconductivity $\Delta\sigma_{xx}$ in the range of ± 0.3 T for 4QL, 7QL, and 11QL nanoplates, respectively. The black arrows indicate the decreasing of the back gate voltage from positive to negative values. Figure 3-16 d-f plot the corresponding Hall resistance at each gate voltage as a function of the magnetic field in ± 3 T. The $R_{xy}(B)$ curves can be linearly fitted (red solid lines), and the sheet carrier concentration n_s can be estimated through the slop R_H as $n_s = -\frac{1}{R_H e}$, as discussed previously. Figure 3-16g the sheet carrier concentration of the three investigated nanoplates under different back gate voltages. The intrinsic sheet carrier density (when $V_g = 0$ V) is in the order of 10^{13} cm^{-2} for all the three nanoplates, slightly higher than MBE grown Bi_2Te_3 thin films.¹¹² The carrier density is in fact over estimated in our system because the Hall-bar geometry with invasive Hall probes used here underestimates the Hall voltage. Also note that the shape and size of the nanoplates can largely affect the measurements, and we therefore only discuss the gate response of the same device instead of comparing different devices. The carrier density can be tuned by a factor of 7 for the 4QL nanoplate from 40 V to -100 V, and a factor of 4 and 2 for the 7QL and 11QL nanoplates, respectively, from 40 V to -80 V. During the back gate tuning range, no carrier density minimum was achieved, suggesting that the Fermi energy still locates above the Dirac point. Ambipolar transport has been realized in Bi_2Te_3 thin films through ionic liquid gate, and also in Bi_2Se_3 thin film

through Al_2O_3 top gate, where the Fermi surface was successfully tuned to the band gap within the surface states.^{112, 196} Our results indicate that a top gate with high refractive index is highly desirable to achieve an effective tuning of the bulk carrier concentration.

Figure 3-16 Gate-dependent (a-c) magnetoconductivity and (d-f) Hall resistance of a 4QL, 7QL, and 11QL Bi_2Te_3 device, respectively. (g) Gate tuning of sheet carrier concentration estimated from Hall measurements. (h-i) Gate tuning of (h) the refraction α and (i) phase coherence length l_ϕ through HLN fitting of the magnetoconductivity.

HLN fitting was conducted for the magnetoconductivity curve at each gate voltage all the three devices. Note that the magnetic range chosen for the fitting is 0.2 T for the 4QL and 7QL devices, while 0.1 T for the 11QL nanoplate due to the big noise in the higher range. The fitted α and l_ϕ as a function of gate voltage are plot in Figure 3-16h and i, respectively. The large values of α up to -2 and even -3 is a result of the inappropriate device geometry. Again, we only focus on the relative change of α and l_ϕ with varying gate voltages within the same device. Previous reports show high sensitivity of α with the effective tuning of the carrier concentration, which was explained by the gate controlled separation between bulk and surface states in a multi carrier channel model.^{185, 196} According to our fitted results, α of the 4QL nanoplate barely changes with a change of carrier concentration by a factor of 7, while α of the 11QL nanoplate can be effectively tuned even though the carrier concentration varies by a factor of 2. One plausible explanation is that the surface and bulk states are spatially mixed in an ultrathin sample (4QL) and behave as one carrier channel during the electron transport. In a thicker sample, such as 11QL, the surface and bulk carriers can be separated through a depletion region by gate and therefore form multi carrier channels.

In this thesis, only very preliminary electron transport data and analysis have been presented. A comprehensive transport study on the gate- and thickness-dependant WAL effect on Bi₂Te₃ nanoplates requires more effort in the Hall device fabrication, such as the improvement on the Hall bar geometry and the employment of the top gate, to achieve an accurate quantitative description and analysis. Further studies on the electron transport properties of Bi₂Te₃ nanoplates will be conducted in the future research.

3.3 Summary

To summarize, high-quality 2D crystals for both transition metal dichalcogenides and bismuth chalcogenides have been successfully prepared, through a mechanical exfoliation method and a vapor transport method, respectively. All the 2D crystals exhibit excellent optical contrast on top of SiO₂/Si substrates, resulted from the optical interference. The high and distinctive optical contrast provides a feasible and convenient method for the fast location and thickness determination of the metal chalcogenide 2D crystals on SiO₂/Si

substrates. Moreover, the vapor transport growth mechanism for the Bi_2Te_3 nanoplates has been comprehensively investigated and a Te-seeded growth model was revealed, where crystalline Te seeds firstly form thermodynamically and then initiate the epitaxial growth of the Bi_2Te_3 nanoplates. The weak anti-localization effect has been observed on the as-grown few-QL Bi_2Te_3 nanoplates through electron transport measurements, as a result of the strong spin-orbit coupling in this topological insulator material.

Chapter 4 Ultralow Frequency Interlayer Breathing and Shear Modes in MX₂ (M=Mo, W; X=S, Se) 2D crystals

4.1 Introduction

Lattice vibrations with ultralow frequencies ($< 50 \text{ cm}^{-1}$) are typically not well investigated through Raman spectroscopy since it is not experimentally trivial. Low frequency Raman spectroscopy is especially interesting in layered materials since a unique type of lattice vibrations resulted for their layered structures, the interlayer phonon modes, can be revealed in this ultralow frequency region. The Brillouin zone center (Γ) interlayer phonon modes represent the vibrations of different vdW layers, where all the atoms within one layer are displacing collectively in the same direction with the same magnitude. Since the weak vdW force is the only restoring force, the frequencies of the interlayer vibrational modes often fall in the ultralow frequency regime ($< 50 \text{ cm}^{-1}$). The Raman observation of the interlayer vibrational modes in bulk layered crystals have been achieved as early as 1970's through triple mode Raman spectrometers, where the in-plane interlayer shear E_{2g}^2 mode was firstly reported at around 42 cm^{-1} in graphite by Nemanich *et al.*,¹⁹⁷ and at around 34 cm^{-1} in bulk MoS₂ by Verble *et al.*¹²⁶ The knowledge of the mode frequencies provided useful information for studying nature of the weak interlayer interactions.

Further investigations on the interlayer lattice vibrations in lower dimensions recently gained people's attention with the outbreak of the 2D crystal research. In 2012, Tan *et al.* studied the interlayer shear E_{2g}^2 mode through Raman spectroscopy in graphene few layers, where they found that the frequency exhibited redshift from with from $\sim 44 \text{ cm}^{-1}$ in graphite to $\sim 31 \text{ cm}^{-1}$ in bilayer graphene, while that of the high-frequency E_{2g}^1 mode (also known as G mode) barely shows any layer thickness dependence. The frequency evolution of the interlayer shear mode was demonstrated as an effective probe to the interlayer vdW force constant, and the lineshape of the E_{2g}^2 Raman peaks indicated strong electron-phonon interactions in the graphene system. At the same time, Michel *et al.* investigated the interlayer phonon properties in few-layer graphene and boron nitride systems, from the

theoretical point of view, where they predicted multiple interlayer vibrational modes with different vibrational symmetries in a given thickness of 2D crystals.¹⁹⁸ In spite of the nice picture provided by experimental and theoretical studies, some mysteries remain uncovered, such as why only one interlayer phonon mode has been observed through Raman spectroscopy among more being predicted to be Raman-active. Another question that would arise inspired by these previous works is that how would the interlayer vibrational modes behave in other layered 2D crystals? And how would they be similar with or different from the few-layer graphene system?

To address the above questions, we present a comprehensive study on the interlayer vibrational properties in the transition metal dichalcogenide 2D crystals in this chapter, through a combination of ultralow frequency Raman spectroscopy, first principles calculations and group theory analysis. Both the interlayer shear and breathing modes are experimentally observed in all the MX_2 ($\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{S}, \text{Se}$) 2D systems. While the frequency of the shear modes exhibits redshifts with decreasing thickness, similar with the case in graphene 2D crystals, the breathing modes follow the opposite trends. Remarkably, the frequency evolutions of these modes can be quantitatively described using a simple linear chain model with only the nearest neighbor interactions, from which both in-plane and out-of-plane interlayer force constants can be derived.

4.2 Raman Spectroscopy Measurements

All the Raman measurements presented in this Chapter were conducted at room temperature in a back scattering geometry using a 100X objective. A 532 nm excitation laser was used for characterizing MoS_2 , MoSe_2 and WSe_2 2D crystals, and a 457 nm excitation laser is used for the WS_2 2D crystals, for non-resonant Raman spectroscopy in the ultralow frequency region. The incident power was kept below 0.5 mW for all the 2D crystals to avoid sample heating. The Raman signal can be selectively detected under certain polarization directions through a half waveplate and a polarizer. Two polarization configurations, $\bar{z}(xx)z$ and $\bar{z}(xy)z$, as discussed in section 2.4.2, were used for the measurements.

4.2.1 Polarization Dependence

Figure 4-1a shows Raman spectra of 1TL, 2TL, 4TL and bulk MoS₂ under both $\bar{z}(xx)z$ (Figure 4-1a) and $\bar{z}(xy)z$ (Figure 4-1b) polarization configurations. Three out of the four Raman-active phonon modes in the bulk are observed around 32 cm⁻¹ (E_{2g}^2), 382 cm⁻¹ (E_{2g}^1) and 407 cm⁻¹ (A_{1g}), respectively, as denoted in the figure. The Raman-active E_{1g} mode, located around 287 cm⁻¹, cannot be observed in our back scattering geometry, as discussed in section 2.4.2. The polarization dependence of these bulk phonon modes are in agreement with our previous phonon symmetry analysis in section 2.4.2, where the in-plane vibrational modes (E_{2g}^2 and E_{2g}^1) are detectable under both parallel ($\bar{z}(xx)z$) and perpendicular ($\bar{z}(xy)z$) polarization configurations, while the out-of-plane A_{1g} mode is largely suppressed under the perpendicular polarization.

From bulk to 1TL, the high frequency E_{2g}^1 and A_{1g} modes exhibit a blue and red frequency shift, respectively, in agreement with a previous report.¹³⁰ In the low frequency region (-55 to 55 cm⁻¹), the Raman-active E_{2g}^2 mode redshifts from ~ 32 cm⁻¹ in bulk to ~ 22 cm⁻¹ in 2TL. Here, we label this mode as S1 since it belongs to an interlayer shear mode where two adjacent TLs vibrate out-of-phase with a phase difference of 180 °. Besides the expected bulk E_{2g}^2 mode, a new broader peak appears in both the Stokes and anti-Stokes spectra of 2TL and 4TL, locating on different sides of the S1 peak, respectively. The polarization dependence of this peak is similar with the high frequency A_{1g} mode, implying that it could correspond to an out-of-plane vibrational mode, and we therefore name it B1 representing breathing mode. Similar new peaks are also observed in few-TL WSe₂ in the low frequency region, as shown in Figure 4-1c and d. The S1 and B1 peaks in WSe₂ are in general of lower frequencies due to its higher molecular weight than that of MoS₂. Interestingly, besides the B1 peak as observed in few-TL MoS₂, another new peak with slightly higher frequency appears in 4TL WSe₂, which exhibits the same polarization dependence as the B1 peak, and we therefore name it B2. It is important to point out that

in the case of 1TL, all the S1, B1 and B2 peaks become absent, implying that they correspond to some interlayer vibrational modes, which is further supported by their ultralow frequency nature. Moreover, based on the polarization properties of the S1, B1 and B2 peaks, we proposed that they correspond to interlayer shear and breathing modes, respectively. The high frequency E_{2g}^1 and A_{1g} mode assignment in WSe₂ is also shown in the right panels of Figure 4-1c and d. Note that the E_{2g}^1 and A_{1g} modes have very close frequencies and cannot be well resolved under the current 532 nm excitation, and we therefore assign them both to the peak located around 250 cm⁻¹, the major contribution to which is in fact the A_{1g} mode. Moreover, the absolute Raman intensities of the E_{2g}^1 & A_{1g} peak or mainly the A_{1g} peak are largely reduced under the $\bar{z}(xy)z$ configuration compared to under the $\bar{z}(xx)z$ configuration, in agreement with its polarization dependence as discussed in section 2.4.2. The high frequency Raman spectra of WSe₂ bulk and 2D crystals will be discussed in detail later in section 5.2.

Figure 4-1 Raman spectra of 1TL, 2TL, 4TL and bulk MoS₂ and WSe₂ under (a, c) $\bar{z}(xx)z$ and (b, d) $\bar{z}(xy)z$ polarization configuration, with 532 nm excitation.

To accurately determine the frequencies and linewidths of the Raman peaks, careful lineshape analysis is necessary. The ultralow frequency Raman spectra are often on top of a background arising in the vicinity of the laser line (0 cm^{-1}), as shown in Figure 4-2a, the Stokes Raman spectrum of 4TL MoS₂. The strong low frequency tail most likely originates from the intraband Raman scattering of free carriers in the n-doped Si substrates,¹⁹⁹ which are highly doped in our experiments with a resistivity of 0.001-0.002 ohm·cm. Under the perpendicular polarization configuration $\vec{z}(xy)\vec{z}$, however, the low frequency background can be largely suppressed, which is consistent with previous reports.^{143, 199}

Figure 4-2 Demonstration of spectrum baseline subtraction and Lorentzian analysis. (a) Raman spectrum of 4TL MoS₂. The black solid line is the original data and the red line is the baseline fitted by a polynomial function. (b) Lorentzian fitting for the baseline-subtracted spectrum (shown as black open circles). Two Lorentzian peaks (green solid line) are used and the red solid line shows the fitting result.

A careful Lorentzian lineshape analysis of the Raman spectrum should start with an appropriate evaluation of the uprising background, which is treated with a polynomial fitting, shown as the red solid line in Figure 4-2a. After the subtraction of the background, a Lorentzian fitting was performed to the spectrum, shown in Figure 4-2b. The red solid line is the fitted result, which matches very well with the experimental data (black open circles). The green solid lines represent the Lorentzian decomposition of the fitting. The accurate Raman peak positions and FWHM intensities can be obtained from the fitting analysis. For the 4TL MoS₂, the S1 peak is found to be located at 29.6 cm^{-1} with a FWHM

of 0.7 cm^{-1} , and the B1 peaks locates at 20.8 cm^{-1} with a FWHM of 1.9 cm^{-1} . In this Chapter, all the discussion on the frequencies and FWHMs of the Raman peaks are based on the lineshape analysis as demonstrated here.

4.2.2 Thickness Dependence

New Raman features have been demonstrated in few-TL MoS₂ and WSe₂ in the ultralow frequency regime and were proposed to correspond to the interlayer vibrational modes, as discussed in the previous section. To better understand these low frequency modes, we next perform a comprehensive Raman investigation with crystal thickness dependence on both materials. Figure 4-3 show the Stokes Raman spectra of 1-12TL and bulk MoS₂ (a-b), as well as 1-7TL and bulk WSe₂ (c-d), measured under both parallel and perpendicular polarization configurations. All the Raman spectra shown here are treated with baseline subtraction and Lorentzian fitting, and are also normalized by the intensity of the strongest S1 peak for a clear demonstration. In MoS₂ 2D crystals, the S1 peak redshifts from $\sim 32 \text{ cm}^{-1}$ to $\sim 22 \text{ cm}^{-1}$ with the thickness decreasing from bulk to 2TL, as guided by the red dashed line (Figure 4-3 a and b). On the other hand, the second strongest peak B1 exhibits blue frequency shift from 9TL ($\sim 10 \text{ cm}^{-1}$) to 2TL ($\sim 40 \text{ cm}^{-1}$) and crosses the redshift trend of the S1 peak at 3TL. Besides the two strong S1 and B1 peaks, two weaker trends of peaks are also observed and labeled as S2 and B2, which are following a redshift and blueshift, respectively, as guided by the red dashed lines in Figure 4-3a. Note that the labeling of the S2 and B2 peaks are based on their polarization dependence, suggesting that they should also correspond to some interlayer shear and breathing modes. The S2 and B2 peaks are much weaker than the S1 and B1 peaks, and therefore are barely distinguishable in Figure 4-3a and b. However, they can be well resolved in the zoom-in spectra.

Figure 4-4 presents the original Raman spectra (without baseline subtraction) for MoS₂ 2D crystals from 3 TLs to 9 TL. Figure 4-4a shows the zoom-in spectra taken under the $\bar{z}(xx)z$ polarization configuration. The B2 peaks can be clearly observed as denoted by the black asterisks from 4TL to 7TL, and scaling from 53 cm^{-1} to 35 cm^{-1} . Following the evolution trend, the B2 peak should be located at even lower frequencies in 8TL and 9TL

and might be masked by the stronger S1 and S2 peaks. The S2 peak is slightly stronger than the B2 peak and shows a smaller FWHM. The red asterisks denote the S2 peaks from 6TL to 9TL. In 4TL and 5TL, the S2 peaks are submerged in the strong B1 peaks measured under the $\bar{z}(xx)z$ polarization configuration, but can be clearly distinguished under the $\bar{z}(xy)z$ polarization configuration (Figure 4-4b), where the breathing modes are suppressed but the shear modes are conserved, as discussed in the previous section. The suppression of the low frequency background under the $\bar{z}(xy)z$ polarization configuration also contributes to the evident exhibition of S2 peaks in the Raman spectra of 4-9TL (Figure 4-4b). So far, the experimental observation of the interlayer shear mode S2 and the interlayer breathing mode B1 has only been unambiguously demonstrated in Few-TL MoS₂.

Figure 4-3 Thickness-dependent low frequency Raman spectroscopy on MoS₂ and WSe₂ 2D crystals with 532 nm excitation. (a-b) Stokes Raman spectra of 1-12TL MoS₂ measured under the (a) $\bar{z}(xx)z$ and (b) the $\bar{z}(xy)z$ polarization configurations. (c-d) Stokes Raman spectra of 1-7TL WSe₂ under the (c) $\bar{z}(xx)z$ and (d) $\bar{z}(xy)z$ polarization configurations.

The experimental data are shown by the blue dots, and the black solid curves represent the Lorentzian fitted results.

Figure 4-4 Zoom-in Raman spectra for the interlayer shear mode S2 and interlayer breathing mode B2 in 3-9TL MoS₂. (a) Original Raman spectra measured under the $\bar{z}(xx)z$ polarization configuration. S2 modes show up as sharp peaks in 6-9TL (denoted by red asterisks), but are masked by the strong B1 peak and Rayleigh background in 5TL and 4TL, respectively. In the higher-frequency region, B2 modes are shown as weak peaks denoted by black asterisks. (b) Original Raman spectra measured under the $\bar{z}(xy)z$ polarization configuration. S2 peaks can be observed distinctly from 4TL to 9TL (denoted by red asterisks). B2 peaks cannot be observed under this configuration.

In comparison, the S2 and B2 peaks are much stronger in WSe₂ 2D crystals, with comparable peak intensities as the S1 and B1 peaks, as shown in Figure 4-3 c and d. Similarly with the case of MoS₂, both the S2 and B2 peaks are observed in 2D crystals with 4TLs or above, while absent in 2TL and 3TL cases. Moreover, in both 2D crystals, the interlayer shear modes (S1 and S2) exhibit red frequency shift, while the interlayer breathing modes (B1 and B2) show blue frequency shift with decreasing crystal thickness. The ultralow frequency Raman peaks are largely dispersed as a function of TL number: In MoS₂, the S1 peak redshifts with a magnitude of $\sim 10 \text{ cm}^{-1}$ from bulk to 2TL, and the B1 peak blueshifts with a magnitude of $\sim 30 \text{ cm}^{-1}$ from 9TL to 2TL. The B1 peak cannot be well resolved in 10TL and above, due to the inadequate signal to noise ratio close to the laser line. In WSe₂, the S2 peaks shows a redshift of $\sim 6 \text{ cm}^{-1}$, and the B1 peaks exhibits a

blueshift of $\sim 20 \text{ cm}^{-1}$ from 7TL to 2TL. The frequency dispersions of E_{2g}^1 and A_{1g} have been proposed as a quick approach to determine the TL number of few-TL MoS_2 ,¹³⁰ where the E_{2g}^1 mode blueshifts with a magnitude of $\sim 3 \text{ cm}^{-1}$ and the A_{1g} mode redshifts $\sim 3.5 \text{ cm}^{-1}$, from bulk to 1TL. In comparison, the ultralow frequency Raman spectroscopy provide a much better route for the crystal thickness determination, thanks to the much higher sensitivity of the peak frequency to the TL number. Remarkably, the distinctive Raman spectra of the 1TL, 2TL and 3TL, in terms of peak number, ensures the high accuracy and convenience of this thickness determination method for 1-3TL 2D crystals, which does not even require a quantitative comparison on the Raman peak frequencies.

Figure 4-5 FWHM of the S1, B1, S2 and B2 Raman peaks as a function of TL number in (a) MoS_2 and (b) WSe_2 2D crystals from Lorentzian lineshape analysis.

The quantitative understanding of the frequency evolutions of the S1, B1, S2, and B2 peaks will be discussed in detail in later sections of this chapter. The linewidths of these peaks extracted from the Lorentzian lineshape analysis of the low frequency Raman spectra are displayed in Figure 4-5 for both MoS_2 and WSe_2 2D crystals. Interestingly, the FWHMs of the in-plane shear modes (S1 and S2) do not show noticeable thickness dependence in both crystals from the bulk to the 2TL case, and are generally around 1 cm^{-1} with a fluctuation of around $\pm 0.5 \text{ cm}^{-1}$. In comparison, the linewidths of the out-of-plane breathing modes (B1 and B2) are much more sensitive to the TL number of the 2D crystals. A remarkable broadening is exhibited by the B1 peak of few-TL MoS_2 , from $\sim 1.8 \text{ cm}^{-1}$ in

9TL to $\sim 6.6 \text{ cm}^{-1}$ in 2TL, as shown in Figure 4-5a. Similarly, a broadening of $\sim 2 \text{ cm}^{-1}$ is also shown by the B1 peaks of few-TL WSe₂ from 7TL to 2TL. The broadening of a Raman peak represents the decrease of the corresponding phonon mode lifetime, as discussed in section 2.3.1, which can be qualitatively understood as a result of the phonon confinement effect or the increased anharmonicity in the 2D limit. It is also important to note that the out-of-plane modes are generally more sensitive to the thickness of the 2D crystals than the in-plane modes, in terms of both frequency and lifetime. This phenomenon can be intuitively understood by the spatial confinement along the out-of-plane z axis, where a larger effect should be played on the out-of-plane lattice vibrations than the in-plane ones when an extra TL is stacked on or removed from the 2D crystal.

Figure 4-6 Thickness-dependent low frequency Raman spectroscopy on MoSe₂ (with 532 nm excitation) and WS₂ (with 457 nm excitation) 2D crystals. (a-b) Stokes Raman spectra of 1-9TL and bulk MoSe₂ measured under the (a) $\bar{z}(xx)z$ and (b) the $\bar{z}(xy)z$ polarization

configurations. (c-d) Stokes Raman spectra of 1-6TL and bulk WSe₂ under the (c) $\bar{z}(xx)z$ and (d) $\bar{z}(xy)z$ polarization configurations.

Ultralow frequency Raman spectroscopy has also been conducted on MoSe₂ and WS₂ 2D crystals with thickness and polarization dependence, as shown in Figure 4-6. Two in-plane shear modes (S1 and S2) can be identified in 2-9TL MoSe₂, which are observed under both the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations, in agreement with the Raman selection rule analysis in section 2.4.2. Both S1 and S2 peaks follow a red frequency shift, consistent with in MoS₂ (Figure 4-3a) and WSe₂ (Figure 4-3c). However, no interlayer breathing modes can be identified in the low frequency region (8-50 cm⁻¹). In 2-6TL WS₂, three trends of peaks are identified as S1, B1 and B2, respectively, as denoted in Figure 4-6c and d.

So far, it has been confirmed that Raman peaks with ultralow frequencies (< 50 cm⁻¹) can be observed in all the four MX₂ 2D crystals, which have been tentatively assigned to the interlayer shear modes (S1 and S2), and interlayer breathing modes (B1 and B2), respectively, according to their polarization dependence. Moreover, the interlayer shear modes follow a redshift while the breathing modes follow a blue frequency shift with decreasing crystal thickness. It is also important to note that in the bulk limit, only the S1 (E_{2g}^2) mode can be identified; while in the 1TL limit, no Raman peaks have been observed at all in the ultralow frequency region. A better understanding of the ultralow frequency Raman spectroscopy, in terms of the correct phonon normal mode assignment, and the frequency evolution trends, requires the support of theoretical analysis.

4.2.3 Substrate Effect

All the Raman spectra discussed in section 4.2.2 were taken on MX₂ 2D crystals samples deposited on top of SiO₂/Si substrates. To investigate the substrate effect, suspended samples were also prepared for the Raman study. A thinner sample should experience a larger substrate effect than a thicker one, if there is any effect, because of its larger surface-to-volume ratio. Here, in terms of investigating the substrate effect on the interlayer

vibrational phonon modes, we study 2TL MoS₂ as an example, which is the thinnest system with Raman-active interlayer vibrational modes.

Figure 4-7a shows the optical image of a 2TL MoS₂ sample on holed 300 nm SiO₂/Si substrates. The holed substrates are prepared by optical lithography followed by HF etching. The etched SiO₂ round holes are around 2.5 μm in diameter and 72 nm in depth. MoS₂ samples are then exfoliated on top of the holed substrates. The thickness of the sample can be determined by the optical contrast of the supported part and by AFM measurements. In Figure 4-7a, the supported and suspended 2TL MoS₂ are denoted by the red and blue arrows, respectively. The Raman spectra of the corresponding areas are displayed in Figure 4-7b, where both the S1 (E_{2g}^2) and B1 peaks are clearly shown. However, there is no observable difference between these two spectra in terms of both peak position and lineshape. Therefore, we conclude that the substrate effect is negligible in our Raman study.

Figure 4-7 Raman spectra of supported and suspended 2TL MoS₂. (a) Optical image of MoS₂ samples on holed 300 nm SiO₂/Si substrates. The round holes are around 2.5 μm in diameter and 72 nm in depth. The supported and suspended 2TL MoS₂ are denoted by red and blue arrows, respectively. (b) Low frequency anti-Stokes and Stokes Raman spectra of supported and suspended 2TL MoS₂ with 532 nm excitation.

4.3 Group Theory Analysis of Phonon Modes in MX₂ 2D Crystals

4.3.1 Crystal Symmetries of Few-TL MX₂

To understand the ultralow frequency Raman spectroscopy, a full picture of the intrinsic phonon properties is necessary. In this section, we present a group theory analysis of the Brillouin zone center phonon normal modes of the MX₂ 2D crystals.

The first step of the group theory analysis is to analyze the point crystal symmetries of the 2D MX₂, as introduced in section 1.3.2. Bulk 2H-MX₂ crystals with infinite TLs belong to the space group D_{6h}^4 ($P6_3/mmc$), as has been studied several decade ago.^{121, 122} For the MX₂ 2D crystals prepared by the mechanical exfoliation method, the /AB/ stacking order of the M and X atomic planes, as shown in Figure 1-2, is believed to keep the same. Compared to their bulk counterparts, the symmetry of the 2D crystals are reduced due to the lack of translation symmetry along the z axis. We next study the allowed symmetry operations in MX₂ 2D crystals. It is important to note that the possession of an inversion symmetry of the 2D crystals with even number of TLs could distinguish themselves from the crystals with odd number of TLs.

Figure 4-8 Symmetry operations in 1TL and 2TL MoS₂/WSe₂. (a-b) Side view (a) and top view (b) of 1TL. (c) Side view of the 1TL unit cell, which includes one Mo atom and two

S atoms. (d-e) Side view (d) and top view (e) of 2TL with /AB/ stacking. The purple spheres denote the sites with two S atoms from the top TL lying on top of one Mo atoms from the bottom TL. The orange spheres stand for the sites with one Mo atom from the top TL lying on top of two S atoms from the bottom TL. (f) Side view of the 2TL unit cell, where four S atoms and two Mo atoms are contained. Each TL is represented a dashed box.

The symmetry operations in few-TLs are demonstrated in Figure 4-8, using 1TL and 2TL as examples for odd- and even-TLs, respectively. The 12 symmetry operations in odd-TLs are: E (identity symmetry), 2 C_3 (the axis of the clockwise and anti-clockwise rotations as denoted by the black lines is shown in Figure 4-8a), 3 C_2' (the three rotation axes are shown in Figure 4-8b as green lines and are lying in the σ_h plane), σ_h (the horizontal reflection plane is represented as the grey plane in Figure 4-8a), 2 S_3 (two C_3 rotations followed by a σ_h reflection), 3 σ_v (one of the vertical reflection planes is represented as the yellow plane in Figure 4-8a). Similarly, the 12 symmetry operations in even-TLs are: E, 2 C_3 (clockwise and anti-clockwise rotations), 3 C_2' (the three rotation axes are shown as the green lines in Figure 4-8e and are lying in the σ_h plane), i (the inversion center is shown as the pink solid circle in Figure 4-8d), 3 σ_d (one of the dihedral reflection planes is represented as the yellow plane in Figure 4-8d, and the top views are shown as the yellow dashed lines in Figure 4-8e), 2 S_6 (clockwise and anti-clockwise C_6 rotations followed by a σ_h reflection). Note that the σ_h reflection alone cannot be considered as a symmetry operation in even-TLs. Consequently, odd-TL crystals belong to the space group D_{3h}^1 ($P\bar{6}m2$) without inversion symmetry, while even-TL crystals belong to the space group D_{3d}^3 ($P\bar{3}m1$) with inversion symmetry.

4.3.2 Irreducible Representations of Phonon Normal Modes

With the point group symmetries of the MX_2 2D crystals, group theory analysis of the Γ phonon normal modes are then conducted, following the steps introduced in section 1.3.2, where 1TL MX_2 has been used as an example to demonstrate the derivation of the irreducible representations of the Γ phonon normal modes: $\Gamma_{1TL} = 2E' + E'' + 2A_2'' + A_1'$.

We next derive the irreducible phonon representations of the 2TL MX₂, which belongs to the point group D_{3d} including the symmetry operations E , $2C_3$, $3C_2'$, i , $2S_6$, $3\sigma_d$, as discussed above. The invariant atomic sites among the 2 Mo sites and 4 S sites under this sequence of symmetry operations are 6, 6, 0, 0, 0, 6, respectively. Consequently, the irreducible representations of $\Gamma_{atom\ sites}$ can be obtained as

$$\Gamma_{atom\ sites} = 3A_{1g} + 2A_{2u}. \quad (4-1)$$

Besides, the irreducible representations of the radial vector can be determined as $\Gamma_{vec} = A_{2u} + E_u$, according to the character table of the point group D_{3h} . Therefore, the irreducible representation of the Γ phonon normal modes in 2TL MX₂ can be obtained as

$$\begin{aligned} \Gamma_{2TL} &= (3A_{1g} + 2A_{2u}) \otimes (A_{2u} + E_u) \\ &= 3A_{1g} + 3A_{2u} + 3E_g + 3E_u. \end{aligned} \quad (4-2)$$

Similarly, we conduct the group theory analysis on all the few-TL cases and obtained such conclusions: the irreducible representations of the zone center phonons can be written as $\Gamma_{odd} = \frac{3N-1}{2}(A_1' + E'') + \frac{3N+1}{2}(A_2'' + E')$, $N = 1, 3, 5, \dots$, where N is the number of TLs; while the phonon irreducible representations for 2D crystals with even number of TLs are $\Gamma_{even} = \frac{3N}{2}(A_{1g} + A_{2u} + E_g + E_u)$, $N = 2, 4, 6, \dots$. On the other hand, the bulk MX₂ crystal belongs to the space group $D_{6h}^4 (P6_3/mmc)$, and irreducible representations of the phonon modes are shown as $\Gamma_{bulk} = A_{1g} + 2A_{2u} + B_{1u} + 2B_{2g} + E_{1g} + 2E_{1u} + E_{2u} + 2E_{2g}$, as discussed in section 1.3.3. The normal mode displacements of 1TL, 2TL and bulk crystals are described in Figure 4-9, where the phonon mode symmetry and Raman/IR activity are denoted in the text underneath the vibration schematics. The two-fold degenerate E modes represent in-plane (shear) vibrations, and the non-degenerate A and B modes vibrate out-of-plane (breathing) along the z axis. Note that the phonon normal modes for 2TL and bulk are the same in terms of quantity and vibrational displacements, since they share the same primitive unit cell. However, the symmetries of the normal modes are different due to their different crystal symmetries, as denoted by the texts beneath the normal modes.

Figure 4-9 Vibrational normal modes of 2H-MX₂. (a) Normal modes of 1TL. (b) Normal modes of 2TL and bulk. The two normal modes in the same column form a pair of Davydov doublets. The mode notations and Raman/IR activities are labelled beneath for both 2TL (in black) and bulk (in purple).

The Raman/IR activities of the zone center phonon modes can also be predicted, according to the character table of the point group that a crystal belongs to, as discussed in section 1.3.2 and section 2.4.2. For the D_{3h} symmetry (odd-TLs), the A'_1 and E'' modes are Raman-active, A''_2 mode is IR-active, and the E' mode is both Raman-active and IR-active. For the group D_{3d} (even-TLs), due to the existence of inversion symmetry, the phonon modes are exclusively Raman-active (A_{1g} , E_g) or IR-active (A_{2u} , E_u). The Raman tensors of the Raman-active vibrational modes in few-TL MX₂ are presented as follows:

$$\begin{aligned}
A'_1 &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \\
E' &: \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
E'' &: \begin{pmatrix} 0 & 0 & -c \\ 0 & 0 & 0 \\ -c & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}
\end{aligned}$$

for 2D crystals with odd number of TLs and

$$\begin{aligned}
A_{1g} &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \\
E_g &: \begin{pmatrix} c & d & 0 \\ d & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & c \\ d & c & 0 \end{pmatrix}
\end{aligned}$$

for 2D crystals with even number of TLs.

It is important to note from Figure 4-9 that the phonon normal modes have similar displacement patterns in crystals with different thicknesses. Each normal mode of 1TL evolves into two modes in 2TL and the bulk limit: each TL in the bulk or 2TL primitive cell is displaced in the same manner as in 1TL, but as a whole the two TLs vibrate either in-phase or out-of-phase, forming Davydov doublets.²⁰⁰ For instance, the acoustic phonon mode E' in 1TL evolves into a Raman-active optical phonon mode E_{2g} and an acoustic mode E_{1u} in the bulk crystal (see their normal mode displacements in the left column of Figure 4-9). Following a similar evolution manner, one normal mode of 1TL will turn into N modes in N TL, keeping the intra-TL displacement while varying the phase difference (0° or 180°) between adjacent TLs. All of the N modes have similar frequencies and thus we call them a *suit*. A pair of Davydove doublets form a phonon *suit* in the bulk limit.

4.3.3 Interlayer Vibrational Modes in MX₂ 2D Crystals

Interlayer vibrations describe the in-phase displacement of all the three atomic layers within a TL. The phase difference among different TLs determines whether the interlayer vibrational mode is optical or acoustic. If all the TLs vibrate in phase (phase difference is 0 °), there is no restoring force either within or among the TLs, and hence the frequency of the normal mode is zero at the Γ point of the Brillouin zone, corresponding to an acoustic phonon mode. On the other hand, a non-zero phase difference among the TLs will result in an interlayer restoring force and hence a non-zero frequency at the Brillouin zone center. In this situation, the vibrations correspond to interlayer optical phonon modes, which we are focusing on in this chapter. In bulk form, there are three optical interlayer modes: a two-fold degenerate Raman-active E_{2g}^2 shear mode and one optically inactive B_{2g}^2 breathing mode. In both modes, two adjacent TLs are vibrating out-of-phase with a 180 ° phase difference, as demonstrated in Figure 4-9b. An NTL crystal has $N-1$ two-fold degenerate interlayer shear modes and $N-1$ non-degenerate interlayer breathing modes. When N is odd, the interlayer breathing modes are either Raman-active (A_1') or IR-active (A_2'') while the interlayer shear modes are either Raman-active (E'') or both Raman-active and IR-active (E'). When N is even, the interlayer breathing modes are either Raman-active (E_g) or IR-active (E_u) and the interlayer shear modes are also Raman-active (A_{1g}) or IR-active (A_{2u}).

Considering the Raman tensors of all the Raman-active modes as shown in section 4.3.2, the polarization properties of the modes in our Raman measurements can be predicted: the interlayer breathing modes A_1' and A_{1g} can be only detectable under the parallel polarization configuration; while the interlayer shear modes E' and E_g can be detected under both parallel and perpendicular polarization configurations. On the other hand, the interlayer shear mode E'' is unobservable at all in the backscattering geometry. The difference in the magnitude of various Raman-active modes stems from the differences in their Raman tensors.

Table 4-1 Interlayer vibrational modes in MX_2 bulk and 2D crystals. The symmetry and Raman/IR activities of the phonon normal modes are listed here. The phonon modes in red are detectable under both the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations while the ones in blue can only be detected under the $\bar{z}(xx)z$ polarization configuration. The phonon modes in black cannot be observed in our Raman measurements.

	Interlayer Shear Modes		Interlayer Breathing Modes	
Bulk	E_{2g}^2 (R)		B_{2g}^2 (Inactive)	
NTL (N-odd)	E' (I+R)	E'' (R)	A_1' (R)	A_2'' (I)
NTL (N-even)	E_g (R)	E_u (I)	A_{1g} (R)	A_{2u} (I)

The group theory analysis for the interlayer vibrational phonon modes in bulk and few-TL MX_2 (NTL) is summarized in Table 4-1. In the bulk limit, only the two degenerate interlayer shear modes can be observed in our backscattering Raman measurements. In NTL crystals, there are $N-1$ two-fold degenerate interlayer shear modes and $N-1$ non-degenerate interlayer breathing modes. Some of the shear modes can be observed under both the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations, as denoted in red; while some breathing modes can only be observed under the $\bar{z}(xx)z$ polarization configuration, as denoted in blue. Those that cannot be observed in our back scattering geometry are denoted in black.

4.4 First Principles Calculations of Phonon Modes

The group theory analysis of the zone center phonon modes has predicted the existence of the $N-1$ interlayer shear and breathing modes, respectively, in a NTL MX_2 2D crystal, which potentially correspond to the experimentally observed Raman peaks (S1, S2 and B1,

B2) with ultralow frequencies, as shown in section 4.2. To have a quantitative description of our experimental observations, in terms of phonon normal mode assignment and phonon frequencies, first principles calculations are conducted for the zone center phonon modes in MoS₂ and WSe₂ 2D crystals.

4.4.1 Calculation Details

First principles calculations of vibrational Raman spectra are performed within density-functional theory (DFT) as implemented in the plane-wave pseudopotential code QUANTUM-ESPRESSO²⁰¹. The local density approximation (LDA)²⁰² to the exchange-correlation functional is employed in the norm-conserving²⁰³ pseudopotential throughout the calculation. For the purpose of comparison, the LDA calculations with projector-augmented wave (PAW)²⁰⁴ potentials for the electron-ion interaction are performed to test the pseudopotential methods. To get converged results, plane-wave kinetic energy cutoffs of 65 Ry and 550 Ry are used for the wave functions and charge density, respectively. The slabs are separated by 16 Å of vacuum to prevent interactions between slabs (this value has been tested for convergence of phonon frequencies). A Monkhorst-Pack k-point mesh of 17×17×5 and 17×17×1 are used to sample the Brillouin Zones for the bulk and thin films systems, respectively. In the self-consistent calculation, the convergence threshold for energy is set to 10⁻⁹ eV. All the atomic coordinates and lattice constants are optimized with the Broyden–Fletcher–Goldfarb–Shanno quasi-Newton algorithm. During the structure optimization, the symmetry of D_{6h}^4 ($P6_3/mmc$) is imposed on the bulk, while the symmetry of D_{3h}^1 ($P\bar{6}m2$) and D_{3d}^3 ($P\bar{3}m1$) is imposed on the odd-TLs and even-TLs, respectively. The structures are considered as relaxed when the maximum component of the Hellmann-Feynman force acting on each ion is less than 0.003 eV/Å.

With the optimized structures and self-consistent wave functions, the phonon spectra and Raman intensities are calculated within density-functional perturbation theory (DFPT) as introduced by Lazzeri and Mauri.²⁰⁵ For the DFPT self-consistent iteration, we used a mixing factor of 0.2 and a high convergence threshold of 10⁻¹⁸ eV. According to the experimental measurement, the LO-TO splitting^{206, 207}, which results from the long range

dipole-dipole interactions associated with long wavelength longitudinal phonons, are included in the calculation with the momentum vector $\mathbf{k}$ approaching zero from the x direction in the dynamical matrix. We find that the LO-TO splitting does not affect the frequencies of the low frequency Raman modes reported in this chapter.

4.4.2 Phonon Normal Mode Assignment

First principles calculations indicate that for a MX_2 2D crystal with N TL, there exist $N-1$ optical interlayer shear modes and $N-1$ optical interlayer breathing modes, all of which have frequencies below 55 cm^{-1} . The phonon mode symmetries and Raman/IR activities can be obtained from the first-principles calculations. Table 4-2 summarizes the calculated number of phonon modes with different symmetry species from 1TL to 9TL, which are consistent with the group theory predicted irreducible representations discussed in section 4.3.2.

Table 4-2 Number of Brillouin zone center phonon modes from the first principles calculations. The Raman-active (R) and IR-active modes (I) are identified.

Modes	R	I	I+R	R
odd (D_{3h})	A'_1	A''_2	E'	E''
1TL	1	2	2	1
3TL	4	5	5	4
5TL	7	8	8	7
7TL	10	11	11	10
9TL	13	14	14	13
Modes	R	I	I	R
even (D_{3d})	A_{1g}	A_{2u}	E_u	E_g
2TL	3	3	3	3
4TL	6	6	6	6
6TL	9	9	9	9
8TL	12	12	12	12

Figure 4-10 Comparison between the experimental (solid spheres) and calculated (open squares) frequencies for the S1, S2, B1 and B2 modes in (a) MoS₂ and (b) WSe₂ 2D crystals.

Moreover, the experimentally observed S1 and S2 Raman peaks correspond to the interlayer shear modes with *highest* and *third-highest* frequencies among the $N-1$ two-fold degenerate shear modes; while the B1 and B2 peaks correspond to the interlayer breathing modes with the *lowest* and *third-lowest* frequencies among the $N-1$ non-degenerate breathing modes. This can account for the fact that the S1 and B1 modes are observed in NTL with $N \geq 2$, while the S2 and B2 modes can only be observed for 4TL and above. According to Table 4-1, the S1 and S2 modes both have a E' symmetry, and the B1 and B2 modes both have a A'_1 symmetry in odd-TLs; while in even-TLs, the interlayer shear (S1 and S2) modes have a E_g symmetry, and the interlayer breathing (B1 and B2) modes have a A_{1g} symmetry. Figure 4-10 displays a direct comparison between the experimental (solid spheres) and calculated frequencies (open squares) for these four modes in both few-TL MoS₂ and WSe₂ are displayed. Overall, the computed LDA frequencies match very well with experiments, with discrepancies of ~ 4 , ~ 1.5 and ~ 2 cm⁻¹ for the S1, B1 and B2 modes, respectively, for MoS₂ and even smaller discrepancies for WSe₂. This good agreement between experiments and calculations confirm our correct phonon mode assignments for these Raman peaks. Note that the no interactions between the substrates and the 2D crystals are considered during the calculations. The good agreement between the experimental and calculated results also suggests that the interactions between the TLs

and the SiO₂/Si substrates are very weak, consistent with our measured results on the suspended samples (see Figure 4-7) and a recent report on frictional properties²⁰⁸.

Figure 4-11 Schematic displacements of the interlayer shear and breathing modes in MoS₂ and WSe₂ bulk and 2D crystals. (a) Vibrational normal modes of the interlayer shear (E_{2g}^2) and breathing modes (B_{2g}^2) in the bulk. (b) Vibrational normal modes of the highest frequency shear mode S1 (top) and the lowest frequency breathing mode B1 (bottom) from 2TL to 9TL. (c) Vibrational normal modes of the third-highest frequency shear mode S2 (top) and the third-lowest frequency breathing mode B2 (bottom) from 4TL to 9TL. The arrow indicates the vibrational direction of a TL and its length is proportional to the

displacement magnitude. The first principles calculated frequencies for MoS₂ and WSe₂ are denoted underneath the phonon normal modes in purple and black, respectively.

The schematic displacements of the experimentally observed phonon normal modes in both bulk and 2D crystals are displayed in Figure 4-11, based on the first principles calculations. The arrows denote the displacement directions of the TLs and their lengths represent the magnitudes of the vibrations. Note that the normal modes are essentially the same for both MoS₂ and WSe₂, except for the absolute frequencies, where the phonon frequency WSe₂ (denoted by the black text) is systematically smaller than that of MoS₂ for (denoted by the purple text) a given phonon normal mode. Figure 4-11a shows the two interlayer vibrational modes in the bulk, where the interlayer shear mode is Raman-active (E_{2g}^2), while the interlayer breathing mode is optically inactive (B_{2g}^2), explaining why only the shear mode are detectable through Raman spectroscopy. The normal mode displacements of the S1 and B1 modes in NTL crystals ($2 \leq N \leq 9$) are schematically shown in Figure 4-11b.

Figure 4-12 Normal mode displacements for all the interlayer shear modes in 2-9TL MX_2 . The normal modes are arranged from low to high frequency, from left to right. The Raman/IR activity is listed below the displacement and the ones highlighted in blue (the highest) and green (the third highest) correspond to the S1 and S2 modes that are observed experimentally, respectively.

Figure 4-13 Normal mode displacements for all the interlayer breathing modes in 2-9TL MX_2 . The normal modes are arranged from low to high frequency, from left to right. The Raman/IR activity is listed below the displacement and the ones highlighted in pink (the lowest) and orange (the third lowest) correspond to the B1 and B2 modes that are observed experimentally, respectively.

A significant characteristic of the S1 mode is the out-of-phase displacements of any adjacent TLs; for the B1 mode, all the TLs are divided into two groups vibrating out-of-phase, while the TLs within each group are displacing in-phase with each other. More out-of-phase vibrations between adjacent layers correspond to a larger restoring force and consequently a larger phonon frequency. The vibrational manners of the S1 and B1 modes as displayed is consistent with S1 being the highest frequency interlayer shear mode and B1 being the lowest frequency interlayer breathing mode. Similar arguments can be made for the fact that the frequency of the S1 mode increases with an increasing number of TLs N , since more out-of-phase displacements are involved in a thicker crystal. On the other hand, a larger N corresponds to a greater proportion of in-phase displacements between adjacent TLs for the B1 mode, and thus results in a lower phonon frequency. Similarly, the smaller frequency of the S2 mode than that of the S1 mode, or the higher frequency of the B2 mode than that of the B1 mode, in a given N TL crystal, as well as their frequency evolutions with crystal thickness, can be understood by the above reasoning.

Besides the experimentally observed S1, S2, B1 and B2 modes as shown in Figure 4-11, we also display the normal mode displacements of all the interlayer shear modes (Figure 4-12) and breathing modes (Figure 4-13) in 2-9TL MX_2 . For a N TL crystal, the displayed phonon normal modes are arranged in a sequence of low to high frequency, from left to right. The Raman/IR activity of each mode is also listed underneath its schematic displacement. The experimentally observed S1, S2, B1 and B2 modes are color coded in blue, green, pink and orange, respectively, to be consistent with the color code in Figure 4-10. Note that among the $N-1$ interlayer shear modes of the N TL crystal, only the modes with the j^{th} -highest ($j=1, 3, 5, \dots$) frequencies can be observed under both the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations. The j^{th} -highest ($j=2, 4, 6, \dots$) frequency modes, however, have a E' symmetry for odd-TLs and a E_u symmetry (IR-active) for even-TLs. As shown in Table 4-1, the E' modes cannot be observed under our back scattering geometry even though being Raman-active. Similarly, only the interlayer breathing modes with the j^{th} -lowest ($j=1, 3, 5, \dots$) frequencies can be observed under the $\bar{z}(xx)z$ polarization configuration, while the one with the j^{th} -lowest ($j=2, 4, 6, \dots$) frequencies are all exclusively IR-active modes, with symmetries of A_2'' for odd-TLs and A_{2u} for even-TLs. These

results are consistent with our experimental observations of the highest, and third-highest frequency interlayer shear modes, as well as the lowest, and third-lowest frequency interlayer breathing modes.

4.4.3 Non-resonant Raman Intensity

In principle, among the $N-1$ interlayer shear or breathing modes of a NTL crystal, the shear modes with the j^{th} -highest ($j=1, 3, 5, \dots$) frequencies, and the breathing modes with the j^{th} -lowest ($j=1, 3, 5, \dots$) frequencies should all be able to be detected through Raman spectroscopy. However, only four modes have been experimentally observed. Also note that the highest frequency shear modes (S1) and the lowest frequency breathing modes (B1) exhibit higher Raman intensities than S2 and B2 modes, especially in MoS₂ and MoSe₂ 2D crystals, as shown in Figure 4-3 and Figure 4-6. To understand the intensity difference between different Raman modes, we conducted the non-resonant Raman calculations.

Within the Placzek approximation²⁰⁹, the components of non-resonant Raman intensity are given by^{205, 210}:

$$R_{ij} \propto \left| \sum_{lm} \frac{\partial^3 E^{el}}{\partial \varepsilon_i \partial \varepsilon_j \partial u_{lm}} \frac{w_{lm}^p}{\sqrt{M_m}} \right|^2 \frac{(\omega_{Laser} - \omega_p)^4}{\omega_p (1 - \exp[-hc\omega_p / k_B T])} \quad (4-3)$$

where E^{el} is the electronic energy of the system, ε_i and ε_j are, respectively, the i -th and j -th Cartesian components of the uniform electric field ε , u_{lm} is the displacement of the m -th atom in the l direction, M_m is the atomic mass of the m^{th} atom, w_{lm}^p is the vibrational eigenmode p of m -th atom in l direction, ω_{Laser} and ω_p are, respectively, the frequencies of the incoming Laser and the p -th vibrational eigenmode. Since $\omega_{Laser} \gg \omega_p$, in practice, we use the formula²⁰⁵

$$R_{ij} \propto \left| \sum_{lm} \frac{\partial^3 E^{el}}{\partial \varepsilon_i \partial \varepsilon_j \partial u_{lm}} \frac{w_{lm}^p}{\sqrt{M_m}} \right|^2 \frac{1}{\omega_p (1 - \exp[-hc\omega_p / k_B T])} \quad (4-4)$$

These intensities are computed within density functional perturbation theory as implemented in Quantum Espresso.

Table 4-3 Calculated phonon frequencies and xx , xy components of the non-resonant Raman intensities for 2TL WSe₂. The symmetry and Raman (R) /IR (I) activity of the modes are identified.

mode	[cm ⁻¹]	R_{xx}	R_{yy}	R_{xy}	symmetry	Activity
1	0	9.48E-18	3.36E-17	1.90E-17	A _{2u}	I
2	0	7.39E-16	1.04E-15	4.11E-15	E _u	I
3	0	1.37E-18	2.44E-18	2.18E-19	E _u	I
4	17.80	1.10E-02	1.10E-02	1.47E-03	E _g	R
5	17.80	1.47E-03	1.47E-03	1.10E-02	E _g	R
6	27.70	4.92E-03	4.92E-03	1.85E-31	A _{1g}	R
7	171.56	4.47E-31	5.18E-31	1.76E-33	E _u	I
8	171.56	5.33E-32	3.26E-32	4.58E-30	E _u	I
9	172.51	6.71E-06	6.71E-06	5.71E-04	E _g	R
10	172.51	5.71E-04	5.71E-04	6.71E-06	E _g	R
11	244.23	3.02E-02	3.02E-02	3.62E-03	E _g	R
12	244.23	3.62E-03	3.62E-03	3.02E-02	E _g	R
13	244.34	7.41E-28	8.23E-28	3.64E-29	E _u	I
14	247.31	2.33E-29	1.69E-29	6.10E-33	E _u	I
15	247.61	3.22E-30	5.83E-31	1.29E-31	A _{2u}	I
16	248.95	8.12E-02	8.12E-02	2.77E-31	A _{1g}	R
17	302.76	6.48E-32	5.80E-32	1.06E-34	A _{2u}	I
18	303.51	1.04E-05	1.04E-05	1.08E-34	A _{1g}	R

The phonon frequencies and Raman intensities of 2TL WSe₂ are given in Table 4-3 as an example, where the shear modes, such as mode 4 and 5, are degenerate, and the R_{xy} of the breathing mode (such as mode 6) is almost zero. Due to the in-plane hexagonal symmetry, both the R_{xx} and R_{yy} components have the same value in all the calculations. The degeneracy of the high-frequency IR shear modes (such as mode 13 and 14) is removed due to the LO-TO splitting. The modes with the highest R_{xx} intensities correspond to those experimentally observed and, consistent with predictions from the group theory, the breathing modes have negligible R_{xy} intensities, consistent with both the group theory analysis and experimental observations.

Consequently, non-resonant Raman intensities of the phonon modes in MoS₂ and WSe₂ 2D crystals are computed by DFT calculations, where the polarization configuration has been taken into consideration with respect to our experimental geometries. The calculated

Raman intensities under the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations are denoted as R_{xx} and R_{xy} , respectively. For the interlayer shear modes, R_{xx} and R_{xy} are of the same orders, while for the interlayer breathing modes, R_{xx} is 10^{28} - 10^{30} times larger than R_{xy} , which suggests that one would expect to observe the breathing mode under a $\bar{z}(xx)z$ configuration, but not for the $\bar{z}(xy)z$ configurations. This is exactly what has been shown in both our group theory analysis and experimental observations (refer to Table 4-1, Figure 4-3 and Figure 4-6). Since both breathing and shear modes can be observed under parallel polarization, we mainly focus on R_{xx} for the following discussion.

Table 4-4 DFT calculated phonon frequency, Raman intensity R_{xx} , normal mode notation and Raman/IR activity of the interlayer shear modes in MoS₂. The modes in blue and in green correspond to the experimentally observed S1 and S2 modes, respectively.

	Frequency (cm ⁻¹) and relative intensity of MoS ₂ shear modes						
bulk	40.0 (1.0)						
	R (E _{2g} ²)						
2 TL	25.8 (1.0)						
	R (E _g)						
3 TL	18.3 (0)	31.3 (1.0)					
	R (E'')	I+R (E')					
4 TL	13.7 (0.1)	25.4 (0)	33.3 (1.0)				
	R (E _g)	I (E _u)	R (E _g)				
5 TL	11.0 (0)	21.2 (0.004)	29.2 (0)	34.3 (1.0)			
	R (E'')	I+R (E')	R (E'')	I+R (E')			
6 TL	9.3 (0.2)	18.0 (0)	25.4 (0.01)	31.2 (0)	34.8 (1.0)		
	R (E _g)	I (E _u)	R (E _g)	I (E _u)	R (E _g)		
7 TL	7.9 (0)	15.5 (0.05)	22.3 (0)	28.0 (0.03)	32.4 (0)	35.3 (1.0)	
	R (E'')	I+R (E')	R (E'')	I+R (E')	R (E'')	I+R (E')	
8 TL	7.2 (0.3)	13.7 (0)	20.0 (0.001)	25.4 (0)	30.0 (0.07)	33.3 (0)	35.4 (1.0)
	R (E _g)	I (E _u)	R (E _g)	I (E _u)	R (E _g)	I (E _u)	R (E _g)
9 TL	6.0 (0)	12.2 (0.06)	17.8 (0)	23.1 (0.0002)	27.5 (0)	31.2 (0.06)	33.9 (0)
	R (E'')	I+R (E')	R (E'')	I+R (E')	R (E'')	I+R (E')	R (E'')

Table 4-4 displays the calculated phonon frequencies, Raman intensity R_{xx} , normal mode notation and the Raman/IR activities for the interlayer shear modes of few-TL and bulk

MoS₂. The highest-frequency shear modes correspond to our experimentally observed S1 mode, as colored in blue. In a given *N*TL, the calculated R_{xx} of all the shear modes are normalized by that of S1, which is the strongest mode. The relative Raman intensities R_{xx} are shown in parentheses, where 0 has a true value of 10^{-28} - 10^{-30} . If we arrange all the shear modes of a certain *N*TL in the order of frequency, some pattern becomes clear: the modes with non-zero R_{xx} are separated by the ones with zero values; and as the phonon frequency becomes smaller, the relative Raman intensity firstly decreases and then increases. The shear modes in green correspond to our experimentally observed S2 modes, whose calculated relative Raman intensities R_{xx} are one or two orders smaller than those of the S1 modes. The Raman intensity calculation predicts that a second interlayer shear mode can be observed only when the thickness is 4 TL and above, which is consistent with our experimental results. For 6TL and 7TL, it is possible to observe a third shear mode; for 8TL and 9TL two more shear modes can be observed besides the S1 and S2 mode. The absence of these modes in our spectra can be explained by their weak Raman intensities or their low frequencies, which are beyond our experimental limit.

Table 4-5 DFT calculated phonon frequency, Raman intensity R_{xx} , normal mode notation and Raman/IR activity of the interlayer breathing modes in MoS₂. The modes in pink and in orange correspond to the experimentally observed B1 and B2 modes, respectively.

	Frequency(cm ⁻¹) and relative intensity of MoS ₂ breathing modes						
bulk	66.1 (1.0)						
	Inactive (B _{2g} ²)						
2 TL	41.4 (1.0)						
	R (A _{1g})						
3 TL	28.8 (1.0)	51.5 (0)					
	R (A' ₁)	I (A'' ₂)					
4 TL	22.3 (1.0)	41.5 (0)	54.0 (0.04)				
	R (A _{1g})	I (A _{2u})	R (A _{1g})				
5 TL	17.1 (1.0)	34.1 (0)	47.5 (0.06)	55.5 (0)			
	R (A' ₁)	I (A'' ₂)	R (A' ₁)	I (A'' ₂)			
6 TL	14.5 (1.0)	29.5 (0)	41.6 (0.08)	50.8 (0)	56.5(0.007)		
	R (A _{1g})	I (A _{2u})	R (A _{1g})	I (A _{2u})	R (A _{1g})		
7 TL	12.9 (1.0)	25.2 (0)	36.3 (0.08)	45.5 (0)	52.6 (0.01)	57.4 (0)	

	R (A'_1)	I (A''_2)	R (A'_1)	I (A''_2)	R (A'_1)	I (A''_2)		
8 TL	10.7 (1.0)	22.3 (0)	32.4 (0.08)	41.0 (0)	48.7 (0.02)	54.2 (0)	57.3 (0.002)	
	R (A_{1g})	I (A_{2u})	R (A_{1g})	I (A_{2u})	R (A_{1g})	I (A_{2u})	R (A_{1g})	
9 TL	9.7 (1.0)	20.0 (0)	29.3 (0.09)	37.6 (0)	45.1 (0.03)	50.8(0)	55 (0.006)	57.5 (0)
	R (A'_1)	I (A''_2)	R (A'_1)	I (A''_2)	R (A'_1)	I (A''_2)	R (A'_1)	I (A''_2)

Table 4-5 presents the calculated phonon frequencies, R_{xx} , and Raman/IR activities for interlayer breathing modes of few-TL and bulk MoS₂. Similar with Table 4-4, all the calculated Raman intensities of the modes in Table 4-5 are normalized by that of the B1 mode, which is the lowest frequency interlayer breathing mode, as colored in pink. The modes colored in orange correspond to the experimentally observed B2 modes. All the breathing modes are either Raman-active with non-zero R_{xx} values or IR-active with zero R_{xx} , consistent with the group theory analysis. For a given NTL, the Raman-active breathing modes are alternating with the IR-active ones in the order of frequency. The calculated Raman intensity R_{xx} of the Raman-active modes becomes smaller as the frequency increases, evolving in a different manner than the interlayer shear modes. The B1 and B2 modes correspond to the first and second strongest Raman-active breathing modes under the $\bar{z}(xx)z$ polarization configuration, qualitatively explaining our experimental observations of only two interlayer breathing modes, even though the experimental intensity ratio of the B2 mode to B1 mode does not match with the DFT calculated result.

For WSe₂, similar calculated results are obtained as in MoS₂. Calculated phonon frequencies, R_{xx} , and Raman/IR activities for interlayer shear modes and breathing modes are presented in Table 4-6 and Table 4-7, respectively. The same color code is used in the tables: S1 modes are highlighted in blue, S2 modes in green, B1 modes in pink and B2 modes in orange. Overall, the Raman intensity calculation qualitatively explains the experimental observations of two interlayer shear modes and breathing modes. In a given NTL, the S1 and S2 modes correspond to the first two highest frequency shear modes among the ones that can be observed under the $\bar{z}(xx)z$ polarization configuration; the B1 and B2 modes correspond to the first two lowest-frequency Raman-active breathing modes.

Table 4-6 DFT calculated phonon frequency, Raman intensity R_{xx} , normal mode notation and Raman/IR activity of the interlayer shear modes in WSe₂. The modes in blue and in green correspond to the experimentally observed S1 and S2 modes, respectively.

	Frequency(cm ⁻¹) and relative intensity of WSe ₂ shear modes					
bulk	24.6 (1.0)					
	R (E _{2g} ²)					
2 TL	17.8 (1.0)					
	R (E _g)					
3 TL	12.4 (0)	21.6 (1.0)				
	R (E'')	I+R (E')				
4 TL	9.4 (0.03)	17.4 (0)	23.0 (1.0)			
	R (E _g)	I (E _u)	R (E _g)			
5 TL	7.5 (0)	14.4 (0.04)	19.9 (0)	23.5 (1.0)		
	R (E'')	I+R (E')	R (E'')	I+R (E')		
6 TL	6.3 (0.005)	12.2 (0)	17.4(0.09)	21.3 (0)	23.9 (1.0)	
	R (E _g)	I (E _u)	R (E _g)	I (E _u)	R (E _g)	
7 TL	5.4 (0)	10.6 (0.005)	15.2 (0)	19.2 (0.07)	22.1 (0)	24.0 (1.0)
	R (E'')	I+R (E')	R (E'')	I+R (E')	R (E'')	I+R (E')

Table 4-7 DFT calculated phonon frequency, Raman intensity R_{xx} , normal mode notation and Raman/IR activity of the interlayer breathing modes in WSe₂. The modes in pink and in orange correspond to the experimentally observed B1 and B2 modes, respectively.

	Frequency(cm ⁻¹) and relative intensity of WSe ₂ breathing modes					
bulk	37.7 (1.0)					
	Inactive (B _{2g} ²)					
2 TL	27.7 (1.0)					
	R (A _{1g})					
3 TL	19.4 (1.0)	33.4 (0)				
	R (A' ₁)	I (A'' ₂)				
4 TL	14.8 (1.0)	27.0 (0)	35.5 (0.04)			
	R (A _{1g})	I (A _{2u})	R (A _{1g})			
5 TL	11.8 (1.0)	22.4 (0)	30.7 (0.08)	36.1 (0)		
	R (A' ₁)	I (A'' ₂)	R (A' ₁)	I (A'' ₂)		
6 TL	9.9 (1.0)	19.1 (0)	27.0 (0.09)	33.0 (0)	36.7 (0.008)	
	R (A _{1g})	I (A _{2u})	R (A _{1g})	I (A _{2u})	R (A _{1g})	

7 TL	8.5 (1.0) R (A'1)	16.5 (0) I (A''2)	23.7 (0.1) R (A'1)	29.6 (0) I (A''2)	34.1 (0.02) R (A'1)	36.9 (0) I (A''2)
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4.5 Linear Chain Model

The mode frequency evolutions as a function of crystal thickness in few-TL MoS₂ and WSe₂ have been well interpreted by the first principles calculations, as shown in Figure 4-10. To have a better understanding of the frequency evolution trends for different interlayer vibrational modes, we developed a linear chain model for a quantitative interpretation.

The schematic of the linear chain model we considered here is shown in Figure 4-14a, where the blue spheres represent the TLs bonded with each other through a spring-like linear force with force constant K . To simplify the model, we only consider the nearest neighbor interactions here and also neglect the interactions between the crystals and the substrates. The force constant K can be broken into an in-plane (K_x) and an out-of-plane (K_z) components, accounting for the interlayer shear and breathing modes, respectively. Note that the force constant K here is for per unit area of TL and therefore the unit of K should be Nm⁻³ instead Nm⁻¹. The linear chain with N spheres has $2N$ degree of freedom, and therefore has N transverse eigenmodes and N longitudinal ones, corresponding to the interlayer shear and breathing modes, respectively.

Solving the linear chain model, the eigenmodes can be obtained as

$$u_j^\alpha \propto \cos \left[\frac{(\alpha-1)(2j-1)\pi}{2N} \right], \quad (4-5)$$

where u_j^α represents the displacement of the j^{th} TL for the α^{th} eigenmode with $\alpha, j = 1, 2, \dots, N$. Consequently, the corresponding frequency of the α^{th} eigenmode (either breathing or shear) of the N TL can be obtained in the unit cm⁻¹ as

$$\omega_\alpha = \sqrt{\frac{K}{2\mu\pi^2 c^2} \left(1 - \cos \left(\frac{(\alpha-1)\pi}{N} \right) \right)}. \quad (4-6)$$

Note that $\alpha = 1$ corresponds to the acoustic mode with zero frequency and $\alpha = 2, 3, \dots, N$ corresponds to the breathing modes ($K = K_z$) or shear modes ($K = K_x$) with frequencies from low to high. μ is the mass per unit area of a MX_2 TL ($\mu = 3.074 \times 10^{-6} \text{ kg/m}^2$ for MoS_2 ; $\mu = 4.473 \times 10^{-6} \text{ kg/m}^2$ for MoSe_2 ; $\mu = 4.969 \times 10^{-6} \text{ kg/m}^2$ for WS_2 ; $\mu = 6.069 \times 10^{-6} \text{ kg/m}^2$ for WSe_2), and c is the speed of light in cm/s. The experimentally observed S1, S2, B1, and B2 modes correspond to the eigenmodes with $\alpha = N, N-2, 2, 4$, respectively. The only free parameter in equation (4-6) is the force constant K , or more specifically K_x for S1 and S2 modes, and K_z for B1 and B2 modes, which can be obtained through the fitting of this equation.

Figure 4-14 Linear chain model interpretation of the frequency evolution trends with varying crystal thickness for the interlayer shear and breathing modes. (a) Schematic of the linear chain model for MX_2 2D crystals. The TLs are represented by the blue spheres and the interlayer interactions are shown as the springs with a force constant K . (b-c) Plots of the S1, S2 and B1, B2 mode frequencies as a function of TL number in (b) MoS_2 and (c) WSe_2 . The experimental data are shown as solid spheres and the calculated results are shown in open squares. The solid lines (red and black) are the fitted results according to the linear chain model.

Figure 4-14b and c show the linear chain model fitting for experimental as well as calculated frequencies of the S1, S2, B1, B2 modes in MoS_2 and WSe_2 2D crystals. The experimental data are displayed in solid spheres and the fitted results according to equation

(4-6) are shown as red solid lines. The calculated frequencies are shown in open squares and the fittings are displayed as black solid lines. The excellent fitting results indicate that the linear chain model interpretation of the frequency evolution trends is quantitatively accurate, which further confirms the correct assignments for these Raman peaks. Moreover, the linear chain model is also applicable in MoSe₂ and WS₂ 2D crystals. Figure 4-15a and b display the experimentally observed Raman peak frequencies as a function of crystal thickness in few-TL MoSe₂ and WS₂, extracted from Figure 4-6. The frequency evolution trends of these peaks can also be well fitted by equation (4-6), as shown by the red solid lines. An important information we can draw from the excellent interpretation through the linear chain model for all the MX₂ 2D crystals is that the interlayer interactions are dominated by the interactions between the nearest neighbor TLs for this family of materials, and the substrate effect is negligible for the 2D crystals prepared by the mechanical exfoliation method.

Figure 4-15 Linear chain model interpretation of the frequency evolution trends with varying crystal thickness for the interlayer shear and breathing modes in (a) MoSe₂ and (b) WS₂ 2D crystals. The solid spheres are experimental data and the red lines are linear chain model fitted results.

Table 4-8 In-plane and out-of-plane force constants (K_x and K_z) per unit area derived from the linear chain model fitting for MoS₂, WSe₂, MoSe₂, and WS₂. The linear chain model predicted frequency for the S1 mode is denoted with the symbol ‡ and values in parentheses

are explicitly calculated by DFT (left column) and measured (right column) through Raman spectroscopy in the bulk crystal.

		DFT (LDA)	Experiment
MoS ₂	$K_z (10^{19} \text{ Nm}^{-3})$	9.26	8.62
	$K_x (10^{19} \text{ Nm}^{-3})$	3.51	2.72
	Bulk S1 frequency (cm^{-1})	36.1 [‡] (35.7)	31.8 [‡] (31.7)
WSe ₂	$K_z (10^{19} \text{ Nm}^{-3})$	8.38	8.63
	$K_x (10^{19} \text{ Nm}^{-3})$	3.41	3.07
	Bulk S1 frequency (cm^{-1})	24.8 [‡] (24.6)	23.5 [‡] (24.0)
MoSe ₂	$K_x (10^{19} \text{ Nm}^{-3})$		2.70
	Bulk S1 frequency (cm^{-1})		26.1 [‡] (26.4)
WS ₂	$K_z (10^{19} \text{ Nm}^{-3})$		9.66
	$K_x (10^{19} \text{ Nm}^{-3})$		3.27
	Bulk S1 frequency (cm^{-1})		27.2 [‡] (27.2)

The in-plane and out-of-plane force constants obtained from the fitting of equation (4-6) in all the four MX₂ 2D crystals are displayed in Table 4-8 for both experimental and calculated data. The K_x (or K_z) derived from fitting the S1 and S2 (or B1 and B2) modes are essentially the same for all the materials, with a discrepancy of less than 1%. K_z derived from fitting the experimental data is almost the same for both MoS₂ and WSe₂ ($\sim 8.6 \times 10^{19} \text{ Nm}^{-3}$), while the value for WS₂ is around 11% larger ($\sim 9.6 \times 10^{19} \text{ Nm}^{-3}$). Note that the K_z cannot be obtained for MoSe₂ since no interlayer breathing modes were experimentally observed. Similar relations also hold for the in-plane (shear) force constant K_x , which is the smallest and very close in MoS₂ and WSe₂, and is the largest in WS₂. K_x demonstrated here for MX₂ is in the same order and a few times larger than that reported in few-layer graphene ($1.28 \times 10^{19} \text{ Nm}^{-3}$).¹⁴³ It is also interesting to note that the out-of-plane force constant K_z is in general around three times as large as the in-plane constant K_x , in MoS₂, WSe₂ and WS₂. With the derived force constant K_x , the frequencies of the S1 mode in the bulk can again be predicted by equation (4-6) and is shown in Table 4-8 for all the four materials, which

agree very well with calculated and experimental S1 frequencies with a discrepancy of less than 0.5 cm^{-1} . The excellent linear chain model fitting using one single parameter K (K_x or K_z) indicates that the inter-TL force constant keeps the same in the bulk or 2D crystals with different thicknesses.

Figure 4-16 Linear chain model and LDA calculated normal mode frequencies with fixed K_x . All the shear modes from 2TL to 9TL MoS₂ can be fitted well by the linear chain model described in the main text. The modes shadowed in blue and green correspond to experimentally observed S1 and S2 modes, respectively.

According to equation (4-6), once the interlayer force constant K is derived from one trend of mode (such as S1), the frequencies of all the interlayer vibrational modes can be obtained in NTL and bulk, thanks to the fact that K is unchanged from 2D to 3D. Using MoS₂ as an example, the derived K_x and K_z through fitting the first principles calculated data are $3.51 \times 10^{19} \text{ Nm}^{-3}$ and $9.26 \times 10^{19} \text{ Nm}^{-3}$, respectively, as shown in Table 4-8. With these two parameters, the frequencies of the interlayer shear and breathing modes in 2-9TL are calculated from equation (4-6), as shown by the open squares in Figure 4-16 and Figure 4-17. As expected, the frequencies predicted by the linear chain model match perfectly with the first principles calculated ones, which are displayed as solid spheres and are mostly covered by the open squares. The S1, S2 and B1, B2 modes are shaded in blue, green, pink, and orange, respectively, consistent with the color code used in Figure 4-14 and Figure 4-15.

Figure 4-17 Linear chain model and LDA calculated normal mode frequencies with fixed K_z . all the breathing modes from 2TL to 9TL MoS₂ can be fitted well by a linear chain model. The modes shadowed in pink and orange correspond to experimentally observed B1 and B2 modes, respectively.

Besides the comprehensive interpretation of the interlayer phonon frequencies, the linear chain model can also give an accurate description of the corresponding normal mode displacements. For a given phonon mode in N TL, the magnitude of the displacement for each TL can be calculated according to equation (4-5). Again, we use the S1, S2 and B1, B2 modes in 9TL MoS₂ as an example. The normalized displacement amplitudes of each TL along the z axis for the B1 (9.7 cm⁻¹) and B2 (29.3 cm⁻¹) modes obtained from our DFT LDA-NC calculations are shown as the solid symbols in Figure 4-18. The open symbols are fitted results through equation (4-5) by setting $\alpha = 2$ and 4, respectively, which match perfectly with the first principles calculations. Similarly, the x direction (in-plane) displacement of each TL for the shear modes S1 (35.5 cm⁻¹) and S2 (31.2 cm⁻¹) can also be perfectly described by equation (4-5) with $\alpha = 9$ and 7, respectively, as shown in Figure 4-19.

Figure 4-18 Spatial distribution of the displacement amplitude for the B1 and B2 modes in 9TL. The LDA calculated data is shown in solid symbols while the model fitting data is depicted in open symbols.

Figure 4-19 Spatial distribution of the displacement amplitude for the S1 and S2 modes in 9TL. The LDA calculated data is shown in solid symbols while the model fitting data is depicted in open symbols.

4.6 Summary

In conclusion, we have uncovered the Raman signature of both interlayer shear and breathing modes in 2H-MX₂ 2D crystals. A full picture of the ultralow frequency interlayer vibrational modes is brought into light through the comprehensive group theory analysis, first principles calculations, as well as the linear chain model interpretation. The existence of the interlayer vibrational modes in few-TL MX₂ and their polarization dependence is predicted by the group theory analysis of zone center phonon modes, which is confirmed by Raman spectroscopy as well as the first principles calculations. The frequency *versus* crystal thickness relations of these interlayer modes can be perfectly characterized by the theoretical calculations, and accurately interpreted through a simple linear chain model. The shear and breathing modes provide effective probes of the interlayer interactions that have important implications for both mechanical and electrical properties. Such ultralow frequency interlayer shear and breathing modes are expected to be universal in all the layered 2D crystals.

Chapter 5 High Frequency Intralayer Vibrational Modes in MX₂ (M=Mo, W; X=S, Se) 2D Crystals

5.1 Introduction

The ultralow frequency ($< 50 \text{ cm}^{-1}$) interlayer vibrational phonon modes in MX₂ bulk and 2D crystals have been investigated theoretically as well as experimentally in chapter 4, we next study the high frequency intralayer modes in these materials, which are much easier to probe through Raman spectroscopy and have been extensively studied.

The first comprehensive Raman study of MX₂ 2D crystals was reported by Lee *et al.* in 2010 on mono- and few-TL MoS₂,¹³⁰ where they found remarkably that the frequency of the intralayer E_{2g}^1 mode exhibits an anomalous blueshift from 3D to 2D, in contrast to the normal redshift of the other intralayer A_{1g} mode. This interesting result invoked extensive theoretical and experimental investigations on the phonon properties of the large family of transition metal chalcogenide, especially their 2D forms.^{55, 131, 132, 211-216} The anomalous lattice vibrations of MoS₂ 2D crystals have been explored by Molina-Sanchez *et al.* with *ab initio* calculations.¹³¹ With a qualitative agreement with the experimental observations, they attributed the anomaly to a dielectric screening enhancement of the long-range Coulomb interactions with increasing the crystal thickness. Yet, a more comprehensive and quantitative description is still lacking. Besides MoS₂, there are also some Raman reports on other MX₂ 2D crystals such as MoSe₂, WS₂, and WSe₂. One common issue for the Raman studies of these materials is that the reported Raman spectra vary a lot in the literatures, due to the resonant Raman scattering effect in the visible and near-IR regime. Consequently, the phonon mode assignment might be difficult with the presence of diverse Raman features with different laser wavelength adopted for the Raman spectroscopy, especially in the on-resonance conditions. For example, there exists a disagreement on the identification of the E_{2g}^1 and A_{1g} modes of mono- and few-TL WSe₂ in different literatures. Sahin *et al.*, Zeng *et al.* and Li *et al.* assigned the A_{1g} mode to a broad feature around 260 cm^{-1} ,^{55, 215, 216} while Zhao *et al.* identified a very weak feature below 250 cm^{-1}

as this mode.¹³² The correct phonon mode assignment of a Raman feature in MX₂ 2D crystals requires a comprehensive study of its polarization and thickness dependence, as well as a quantitative comparison with the theoretical predictions.

In this chapter, we report a comprehensive Raman spectroscopy study of MX₂ bulk and 2D crystals in the high frequency region (50-500 cm⁻¹), where the characteristic intralayer E_{2g}^1 and A_{1g} modes are identified clearly with appropriate excitation wavelengths. The anomalous lattice vibrations, blueshift of the E_{2g}^1 mode frequency with decreasing thickness, is universal in all the four MX₂ 2D crystals, which can be quantitatively explained as a result of the surface effect, as demonstrated by the first principles calculations. Moreover, some Raman-inactive phonon modes of the bulk have been identified in the Raman spectra of MX₂ 2D crystals under certain conditions. The experimental observations of these unexpected Raman features can be attributed to a Raman-inactive to Raman-active transition of the phonon modes as a result of lowered crystal symmetry and dimensionality in 2D. Our results shed light on a general understanding of the phonon properties of MX₂ and their behaviors from 3D to 2D.

5.2 Thickness Dependent Raman Measurements

Raman spectroscopy of MX₂ bulk crystals and the phonon normal mode assignment have been conducted several decades ago.^{122, 126, 217, 218} Recall (section 1.3.3) that there exist four Raman-active phonon normal modes in the MX₂ bulk crystal, one low frequency interlayer shear mode (E_{2g}^2) and three high frequency intralayer vibrational modes (E_{1g} , E_{2g}^1 and A_{1g}). The experimentally observed frequencies of these intrinsic Raman-active bulk phonon modes in the four MX₂ materials are extracted from current existing literatures and summarized in Table 5-1. Note that the observation of the E_{1g} mode requires the probe of zx or zy components of its Raman tensor (refer to section 1.3.3) and has often been realized in a *right angle scattering* geometry where the incident light is almost parallel to the crystal plane. Moreover, the E_{1g} Raman peak is two or three orders weaker than the

E_{2g}^1 and A_{1g} peaks in MoS₂ and WSe₂, while being comparable with the A_{1g} peak in MoSe₂. In bulk WS₂, the E_{1g} mode has not been identified through Raman spectroscopy to the best of our knowledge and is theoretically predicted to be around 306 cm⁻¹.²¹⁹

Table 5-1 Summary of the observed frequencies of the four intrinsic Raman-active phonon modes in MX₂ bulk crystals. All the data are obtained through Raman spectroscopy in current existing literatures (MoS₂,^{122, 126} MoSe₂,²¹⁷ WS₂,²¹⁹ WSe₂²¹⁸) except for the theoretically predicted frequency of the E_{1g} mode in WS₂, as denoted by the asterisk.

Raman-active Phonon Modes (cm ⁻¹)				
	E_{2g}^2	E_{1g}	E_{2g}^1	A_{1g}
MoS ₂	34	287	383	409
MoSe ₂	27	169	283	243
WS ₂	27	306*	357	423
WSe ₂	25	178	250	253

To clearly identify the high frequency intralayer vibrational modes in MX₂ 2D crystals, systematic thickness and polarization dependence Raman measurements have been conducted. The excitation wavelength is 532 nm for MoS₂ and MoSe₂, 457 nm and 633 nm for WS₂ and WSe₂, respectively, with an incident power below 0.5 mW. Figure 5-1 shows the Raman spectra of 1-12TL MoS₂ and 1-6TL WS₂ under both $\bar{z}(xx)z$ (a and c) and $\bar{z}(xy)z$ (b and d) polarization configurations. The E_{2g}^1 and A_{1g} modes can be clearly identified with bulk frequencies consistent with previous reports. The E_{1g} mode cannot be observed under our back scattering geometry as discussed in section 2.4.2. The polarization dependence of the E_{2g}^1 and A_{1g} peaks show consistency with the ultralow frequency interlayer modes, where the out-of-plane vibrations (B) are suppressed under the perpendicular polarization configuration while the in-plane vibrational modes (S) remained.

A quantitative description of this polarization dependence can also be understood through the symmetry selection rule (section 2.4.2). In both MoS₂ and WS₂, the E_{2g}^1 mode exhibit a blue frequency shift while the A_{1g} redshifts with decreasing crystal thickness, as guided by the red dashed lines. Moreover, the A_{1g} peaks exhibit distinctive broadening from 3D to 2D, which will be discussed in detail later.

Figure 5-1 Raman spectra of (a, b) 1-12TL and bulk MoS₂ with 532 nm excitation and (c, d) 1-6TL and bulk WS₂ with 457 nm excitation.

Figure 5-2 Raman spectra of (a, b) 1-9TL and bulk MoSe₂ with 532 nm excitation and (c, d) 1-7TL and bulk WSe₂, with 633 nm excitation.

Similar thickness and polarization dependent Raman spectra for MoSe₂ and WSe₂ bulk and 2D crystals are shown in Figure 5-2. Unlike the strong E_{2g}^1 peak in MoS₂ and WS₂, the E_{2g}^1 mode (denoted by the asterisk in Figure 5-2a and b) appears very weak in MoSe₂ and can barely be distinguished under both $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations. The E_{2g}^1 mode in WSe₂ is also very weak, appearing as a little hump on the left shoulder of the A_{1g} peak (Figure 5-2c), while can be clearly identified under the perpendicular polarization configuration (Figure 5-2d). Note that the A_{1g} mode is not expected under the $\bar{z}(xy)z$ configuration, and its appearance here is due to the

experimental limitation, where the analyzer (polarizer) cannot completely eliminate the signal with unwanted polarizations, such as the A_{1g} Raman signal in this case. However, the much suppressed intensity of the A_{1g} peak compared to the E_{2g}^1 peak is a good evidence of its polarization dependence. The broad Raman feature located around 260 cm^{-1} has been attributed to a two phonon scattering process involving the longitudinal acoustic phonon at the M point of the Brillouin zone,²¹⁴ and is denoted as $2LA(M)$. There has been lacking a consensus of the E_{2g}^1 and A_{1g} mode assignment in WSe₂ 2D crystals. The main reason is that these two Raman peaks have very close frequencies (difference $< 3\text{ cm}^{-1}$) while at the same time very different intensities, which makes them difficult to be well resolved in the Raman spectra. Consequently, the $2LA(M)$ Raman feature has been mistaken as the A_{1g} mode occasionally.^{55, 216, 220} In our Raman spectra, the distinctly resolved E_{2g}^1 and A_{1g} Raman peaks and their polarization dependences provide a solid evidence on the correct phonon mode assignment. Note that in the limit of 1TL WSe₂, the two peaks are almost degenerate and merge as a single peak in our Raman spectra (Figure 5c and d). The frequency evolutions of the E_{2g}^1 and A_{1g} modes as a function of crystal thickness in MoSe₂ and WSe₂ 2D crystals follow the same trends as in MoS₂ and WS₂, redshift and blueshift, respectively, with decreasing number of TLs.

By far, the high frequency intralayer vibrational E_{2g}^1 and A_{1g} modes have been clearly identified in the Raman spectra of MX₂ bulk and 2D crystals. In all the four materials, the in-plane shear mode E_{2g}^1 experiences a frequency hardening from 3D to 2D, while the out-of-plane breathing mode A_{1g} exhibits a frequency softening.

5.3 Anomalous Lattice Vibrations in MX₂ 2D Crystals

5.3.1 Frequency and Linewidth Evolutions from 3D to 2D

The thickness dependence of the E_{2g}^1 and A_{1g} Raman peaks in MX₂ bulk and 2D crystals have been demonstrated in the previous section, we next conduct a quantitative

description of their frequency and linewidth evolutions from 3D to 2D through a lineshape analysis. Figure 5-3 shows the multi-Lorentzian fitting of the intralayer E_{2g}^1 and A_{1g} peaks using the 2TL MoS₂ and 2TL WSe₂ as examples. Note that four individual Lorentzian peaks are used to achieve a good fitting in 2TL MoS₂, as shown in Figure 5-3a. The two strong peaks correspond to the E_{2g}^1 and A_{1g} modes, respectively, and we tentatively attribute the two minor peaks to some high-order phonon scattering processes and will not discuss them in detail here. The Raman spectra taken under the $\bar{z}(xy)z$ polarization configuration are chosen for the fitting in 2TL WSe₂ (Figure 5-3b) since the E_{2g}^1 and A_{1g} peaks are better resolved in this case with comparable intensities, which is favorable for the fitting analysis.

Figure 5-3 Multi-Lorentzian fitting of for the Raman spectra of (a) 2TL MoS₂ taken under $\bar{z}(xx)z$ polarization configuration and (b) 2TL WSe₂ taken under $\bar{z}(xy)z$ polarization configuration, with 532 nm excitation. The black dots are experimental Raman spectra and the red lines are fitted results. The green lines represent the individual Lorentzian peaks used for the fitting.

Multi-Lorentzian fitting as demonstrated above are conducted for all the four MX₂ materials with different thickness, from which the frequencies and linewidths of the E_{2g}^1 and A_{1g} peaks are extracted and displayed as Figure 5-4 and Figure 5-5, respectively. The E_{2g}^1 peak exhibits a blueshift of ~ 3.3 cm⁻¹, ~ 2.9 cm⁻¹, and ~ 1.3 cm⁻¹ from bulk to 1TL in

MoS₂, WS₂ and WSe₂, respectively. On the other hand, the frequencies of the A_{1g} peaks in 1TL shows a redshift of $\sim 3.6 \text{ cm}^{-1}$, $\sim 1.1 \text{ cm}^{-1}$, $\sim 2.0 \text{ cm}^{-1}$, and $\sim 1.3 \text{ cm}^{-1}$ with respect to that in the bulk for MoS₂, WS₂, MoSe₂ and WSe₂, respectively. Since the observed frequencies of the phonon modes depend on the alignment of the Raman spectrometer and the excitation laser wavelength, there often exist some discrepancies of around a few cm^{-1} in different reports. Therefore, the frequency difference between the E_{2g}^1 and A_{1g} peaks can serve as a better reference for determining 2D crystal thickness than using the absolute frequencies of either peak, as first proposed by Lee *et al.* in MoS₂ 2D crystals.¹³⁰

Figure 5-4 Frequency evolutions as a function of TL number for the the E_{2g}^1 and A_{1g} peaks in (a) MoS₂, (b) WS₂, (c) MoSe₂, and (d) WSe₂ 2D and bulk crystals. Note that MoS₂, MoSe₂ are excited by a 532 nm laser, WSe₂ is excited by a 633 nm laser, and WS₂ is excited by a 457 nm laser. The frequencies of the two peaks are referring to the y axis on the left,

as denoted by the red and blue arrows, and their frequency differences (black open squares) are also shown with respect to the y axis on the right, as denoted by the black arrows.

The dispersion relations between the frequency difference and TL number are also shown in Figure 5-4 as the black open squares with respect to the y axis on the right hand side. The E_{2g}^1 and A_{1g} frequency difference increases by a magnitude of $\sim 3.1 \text{ cm}^{-1}$, $\sim 1.5 \text{ cm}^{-1}$ and $\sim 1.5 \text{ cm}^{-1}$ from 1TL to 2TL in MoS_2 , WS_2 , and WSe_2 , respectively, and the increase step gets smaller and more difficult to distinguish with increasing thicknesses. However, the thickness determination through this technique has been demonstrated to be effective for 1-3TL 2D crystals. In comparison, ultralow frequency Raman spectroscopy functions much better in terms of TL number determination with high accuracy up to 6TL (refer to section 4.2.2), although technically more difficult.

The FWHMs for the E_{2g}^1 and A_{1g} peaks extracted from the Lorentzian fittings are shown in Figure 5-5 for the four MX_2 bulk and 2D crystals. In MoS_2 , the line width of the A_{1g} peak monotonically increases from bulk ($\sim 2.6 \text{ cm}^{-1}$) to 3TL ($\sim 6.0 \text{ cm}^{-1}$), and the E_{2g}^1 peak also shows a slight broadening from bulk to 3TL of around 1 cm^{-1} . The broadening trends with decreasing thickness, however, stop at 3TL with opposite evolution trends from 3TL to 1TL, which are mostly consistent with previous report from Lee *et al.*¹³⁰ The linewidth behaviors of the A_{1g} and E_{2g}^1 peaks in WS_2 are very similar with in MoS_2 , except that the broadening effect of the A_{1g} peak is from the bulk all the way till 1TL, and the slight narrowing effect appears from 2TL for the E_{2g}^1 peak. Note that in both MoS_2 and WS_2 , the FWHM of the A_{1g} peak is larger than that of the E_{2g}^1 peak, especially in the extreme 2D regime. In MoSe_2 , the broadening effect of the A_{1g} peak is not as distinct as in MoS_2 and WS_2 , with a magnitude of $\sim 0.8 \text{ cm}^{-1}$ from bulk to 1TL. In the case of WSe_2 , however, we cannot observe distinctive broadening effect in either Raman peak, probably due to the small FWHMs for both peaks ($1\text{-}2 \text{ cm}^{-1}$) as well as the relative larger fitting errors. Considering the experimental and fitting errors, we can draw a conclusion from the results shown in Figure 5-5 that, overall, both the A_{1g} and E_{2g}^1 peaks experience a

linewidth broadening from 3D to 2D, and the FWHM of the former is more sensitive to the thickness of the 2D crystal than that of the latter.

Figure 5-5 Linewidth evolutions as a function of TL number for the the E_{2g}^1 and A_{1g} peaks in (a) MoS₂, (b) WS₂, (c) MoSe₂, and (d) WSe₂ 2D and bulk crystals, as shown by the blue and red spheres, respectively. Note that MoS₂, MoSe₂ are excited by a 532 nm laser, WSe₂ is excited by a 633 nm laser, and WS₂ is excited by a 457 nm laser.

The overall broadening effect of the E_{2g}^1 and A_{1g} peaks from bulk to 2D can be qualitatively understood by the phonon confinement effect and the uncertainty rule, as discussed in section 2.6. The uncertainty rule relates the position and momentum, $\Delta x \cdot \Delta p \approx h$. Here $\Delta p \approx (\hbar/2\pi)\Delta q$, Δx is the material size. In the bulk limit, $\Delta x \rightarrow \infty$ and $\Delta q \rightarrow 0$, so only zone-center (Γ point) phonons can be experimentally observed. When

both Δx and Δq have finite values, phonons in the vicinity of Γ point will also get involved in Raman scattering, causing a phonon frequency shift and line width broadening, and this is known as the phonon confinement effect. The broadening of a Raman peak also corresponds to a decreased phonon lifetime in 2D, in which case the scattering process involves phonons with different phases and momentums, instead of only Γ phonons in the bulk. The phonon confinement effect gets more dominant when the sample size gets closer to the 2D limit. The large thickness dependence of the A_{1g} line width is related to its out-of-plane vibration manner, along which direction the size of the sample is largely confined. Meanwhile, it is not difficult to understand why the E_{2g}^1 mode is less affected considering the fact that the atoms are vibrating in plane and the lateral size of the sample is not much confined from bulk to 2D.

Contradictory to the expected phonon confinement effect, the E_{2g}^1 and A_{1g} peaks in MoS_2 , as well as the E_{2g}^1 peak in WS_2 exhibit a slight narrowing effect from 2-3TL down to the extreme 2D limit of 1TL. One plausible explanation for this anomalous phenomenon is the special electronic structure of 1TL MX_2 . As has been introduced in section 1.2.1, the band gap of MX_2 experiences an indirect-to-direct transition from bulk to monolayer. Therefore, the phonon-electron interactions in 1TL will be very different from 2TL and above. For example, in the indirect band gap cases (2TL and above), phonons with large momentum are largely involved in the photon absorption, emission and phonon scattering processes. While in 1TL, large momentum phonons would not be involved as much given the fact of a direct band gap system. The scattering of phonons with different momentums (and thus phases) would result in a reduced lifetime, thus it is reasonable to assume that the lifetime of phonons in 1TL should be longer than thicker 2D crystals. The linewidth evolutions of E_{2g}^1 and A_{1g} modes are determined by both the phonon confinement effect and the involvement of large momentum phonons during the scattering process. The latter should be less dominant in 1TL, thus giving smaller linewidths in 1TL than in 2TL. Such a reasoning based on the electronic structure of 1TL MX_2 only provides a certain degree of insights on the narrowing effect of the Raman peaks at the extreme 2D limit, and a deeper understanding of the mechanism behind requires further investigations.

5.3.2 First Principles Calculations of Intralayer Phonon Modes

To further investigate the physical mechanisms that govern the anomalous lattice vibrations in the MX₂ 2D crystals, we next conduct a first principles study on the Γ phonon frequencies and their evolution trends as a function of crystal thickness. A detailed analysis will be presented using MoS₂ and WSe₂ as examples, the conclusion drawn from which should be applicable to the other two MX₂ crystals.

First principles calculations are performed using DFT as implemented in the plane-wave pseudopotential code QUANTUM-ESPRESSO.²²¹ Different DFT exchange-correlation functionals have been chosen and compared for the study, such as the LDA,²⁰² a semiempirical vdW correction based on Grimme's scheme (PBE-D2),²²² as well as the vdW density functional (vdW-DF)²²³ with Cooper's exchange.²²⁵ Our results indicate that the LDA calculations give the best agreement with the experimental results,²²⁴ as has been demonstrated in our first principles study of the ultralow frequency interlayer phonon modes in chapter 4,²²⁰ which is also consistent with other studies on the layered 2D crystals.²²⁵⁻²²⁸ Despite that the LDA functional does not explicitly include the inter-TL vdW interactions, as the vdW-DF, it best describes the force constants and normal mode frequencies. Therefore, in this section, we focus on the LDA calculations, where a plane-wave kinetic energy cutoff of 65 Ry is used to get converged results. For the few TL system, neighboring slabs are separated by a vacuum thickness of 16 Å (this value has been tested for convergence of phonon frequencies). The Monkhorst-Pack k-point mesh of 17×17×5 and 17×17×1 are used to sample the Brillouin Zones for bulk and thin film systems, respectively. In the self-consistent calculation, the convergence threshold for energy is set to 10⁻⁹ eV. All the atomic coordinates and lattice constants are fully relaxed until the absolute value of force acting on each atom is less than 0.003 eV/Å. During the structure optimization, the hexagonal symmetry is imposed on the bulk and few TL systems. With the optimized structures and self-consistent wave functions, the phonon spectrum and Raman intensities are calculated within density-functional perturbation theory (DFPT) as introduced by Lazzeri and Mauri.²²⁹ Non-resonant Raman intensities ($\omega_{Laser} \gg \omega_p$) of the Γ phonon modes are calculated within the Placzek approximation²²⁹, as discussed in section 4.4.3. Since both the E_{2g}^1 and A_{1g} modes can be observed under the $\bar{z}(xx)z$ polarization

configuration, their Raman intensities under this configuration (I_{xx}) are computed in this chapter to show consistency with experiments.

Figure 5-6 (a) Top view of the crystalline structure of 2H-MoS₂. The primitive unit cell is denoted by the grey dashed diamond. (b) Side view of the primitive unit cell composed of two TLs and its corresponding linear chain schematic with interatomic force constants up to the second nearest neighbors. (c) Displacement schematics of all the zone center vibrational phonon modes and their frequencies from LDA calculations. Each column of the phonon normal modes forms a Davydov doublet.

Recall that the primitive unit cell of bulk MX₂ overruns two TLs and is composed of six atoms, as displayed in Figure 5-6a and b. Therefore, there exist 18 Γ phonon modes and their irreducible representations are $\Gamma_{bulk} = 2A_{2u} + 2E_{1u} + 2B_{2g} + 2E_{2g} + A_{1g} + E_{1g} + B_{1u} + E_{2u}$, with twelve in-plane vibrational modes (E) and six out-of-plane vibrational modes (A and B), as discussed in section 1.3.3. Note that all the in-plane E modes are two-fold degenerate and therefore they exhibit six different frequencies. The displacement schematics of all bulk phonon modes have been displayed in Figure 5-6c. As analysed in section 4.3.1, a NTL MX₂ 2D crystal has $9N$ Γ phonon modes and the irreducible representations are

$$\Gamma_{even-TL} = \frac{(3N-1)}{2} (A_1' + A_2'' + E' + E'') + A_2'' + E', N = 1, 3, 5... \quad \text{for even-TLs and}$$

$$\Gamma_{odd-TL} = \frac{3N}{2} (A_{1g} + A_{2u} + E_g + E_u), N = 2, 4, 6... \quad \text{for odd-TLs. Table 5-2 displays all the}$$

LDA calculated Γ phonon frequencies and their relative Raman intensities (I_{xx}) in 1-4TL and bulk MoS₂. Similarly, the calculated results for bulk and 1-4TL WSe₂ are shown in Table 5-3. The irreducible representations of the phonon modes and their Raman/IR activities obtained from the calculation are also shown in the tables.

The phonon evolution rule discussed in section 4.3.1 can be well demonstrated by the calculated results shown in Table 5-2 and Table 5-3. Each normal mode of 1TL evolves into N modes in N TL with very close frequencies, which can be referred to as a *suit*. A *suit* of phonon modes share the same lattice displacements within one TL, while the inter-TL displacements vary. The phonon modes in N TL and bulk MX₂ that share the same origin in 1TL are shaded using the same color in Table 5-2 and Table 5-3. Taking MoS₂ for an example, the A_1' mode (406.1 cm⁻¹) in 1TL evolves into a A_{2u} mode (405.5 cm⁻¹) and a A_{1g} mode (407.6 cm⁻¹) in 2TL, as shaded in pink; in 3TL, this *suit* of modes become a A_1' mode (405.9 cm⁻¹), a A_2'' mode (406.5 cm⁻¹), and another A_1' mode (407.9 cm⁻¹). In the bulk limit, the *suit* that originates from the A_1' mode in 1TL turn into a B_{1u} mode (404.0 cm⁻¹) and a A_{1g} mode (408.1 cm⁻¹), which are also known as a Davydov doublet.²⁰⁰ Since 1TL MX₂ has six phonon normal modes, there exist six *suits* of phonon modes in N TL, with each *suit* composed of N phonons; and in bulk, there exist six pairs of Davydov doublets.

The reason that a *suit* of phonon modes in a given N TL have similar frequencies lies in the weak inter-TL vdW interactions. As shown in Figure 5-6c, the only different between a Davydov doublet is that the inter-TL vibration, which is either in-phase (such as the B_{1u} mode), or out-of-phase with a phase shift of 180° (such as the A_{1g} mode). Intuitively, the out-of-phase displacement corresponds to a larger restoring force and consequently a higher frequency of the corresponding phonon mode, which can be demonstrated by a simple oscillator model with the consideration of only the vdW interactions between two adjacent TLs.^{200, 230} In our calculations, this trend can also be predicted among five of the

six Davydov doublets- (E_{2g}^2, E_{1u}^1) , (B_{2g}^2, A_{2u}^1) , (E_{1g}, E_{2u}) , (E_{2g}^2, E_{1u}^1) , (A_{1g}, B_{1u}) , and (B_{2g}^1, A_{2u}^2) . The frequency difference between the Davydov doublet, also known as the Davydov splitting, is only a few cm^{-1} for the intralayer vibrational modes, but can be as large as tens of cm^{-1} for the intralayer vibrational modes where the inter-TL being the only restoring force. The sixth pair of doublet (E_{2g}^1, E_{1u}^2) , however, was experimentally found to follow an anomalous frequency trend with $\omega(E_{1u}^2) \sim 1 \text{ cm}^{-1}$ larger than $\omega(E_{2g}^1)$ through Raman and IR spectroscopy,¹²¹ which has been accurately captured by our LDA calculations on both MoS₂ and WSe₂ (Table 5-2 and 5-3). Similar anomalous Davydov splitting has also been observed in other layered materials such as GaS, GaSe, As₂Se₃, *etc.*,^{231, 232} and were interpreted through the long-range Coulomb interactions. Our LDA calculations of MoS₂ indicate that the in-plane force constant between the Mo and S atoms within two adjacent TLs (k_{Mo-S-2}) is about 40% larger than the inter-TL vdW interaction that is mainly contributed by the S-S force constant within two TLs (k_{S-S-1}), as shown in Figure 5-6b. Consequently, compared to the E_{2g}^1 mode, the larger second nearest neighbor Mo-S interactions (k_{Mo-S-2}) in the E_{1u}^2 mode over compensates the smaller nearest neighbor S-S interactions (k_{S-S-1}) and overall result in a larger restoring force. Therefore, Coulomb interactions between the Mo and S atoms up to the second nearest neighbors are important for accounting for the abnormal Davydov splitting between the in-plane E_{2g}^1 and E_{1u}^2 modes. Similar reasoning can also be made to WSe₂.

Table 5-2 LDA calculated results for the Γ phonons in 1-4TL and bulk MoS₂. The phonon frequencies (cm^{-1}) and relative Raman intensities I_{xx} (in parentheses) are listed in the first and second row, respectively, in each cell. The Raman intensity I_{xx} is normalized by the largest value in each row. The irreducible representations of the phonon modes and their corresponding optical activities (in square brackets) are listed as the third row of each cell. R represents Raman-active, I represents IR-active and S stands for silent or optically inactive. The phonon modes highlighted in red correspond to the experimentally observed intralayer E_{2g}^1 and A_{1g} modes. The phonon modes shaded in the same color originate from the same phonon mode of 1TL and have similar frequencies.

In-plane Modes	bulk	0 (0) E_{1u}^1 [I]	35.7 (0.31) E_{2g}^2 [R]	285.2 (0) E_{2u} [S]	287.8 (0) E_{1g} [R]	384.9 (1.0) E_{2g}^1 [R]	385.7 (0) E_{1u}^2 [I]						
	1 TL	0 (0) $E' [I+R]$	287.4 (0) $E'' [R]$	389.0 (1.0) $E' [I+R]$									
	2 TL	0 (0) E_u [I]	25.8 (0.06) E_g [R]	286.4 (0) E_u [I]	287.8 (0.02) E_g [R]	387.14 (1.0) E_g [R]	387.5 (0) E_u [I]						
	3 TL	0 (0) $E' [I+R]$	18.3 (0) $E'' [R]$	31.3 (0.24) $E' [I+R]$	285.9 (0) $E'' [R]$	287.0 (0.02) $E' [I+R]$	287.8 (0) $E'' [R]$	385.4 (1.0) $E' [I+R]$	387.19 (0) $E'' [R]$	387.23 (0.76) $E' [I+R]$			
	4 TL	0 (0) E_u [I]	13.7 (0.03) E_g [R]	25.4 (0) E_u [I]	33.3 (0.29) E_g [R]	285.7 (0) E_u [I]	286.5 (0.006) E_g [R]	287.4 (0) E_u [I]	287.9 (0.006) E_g [R]	385.2 (1.0) E_g [R]	385.6 (0) E_u [I]	387.27 (0.42) E_g [R]	387.28 (0) E_u [I]
Out-of-plane Modes	bulk	0 (0) A_{2u}^1 [I]	57.9 (0.0) B_{2g}^2 [S]	404.0 (0) B_{1u} [S]	408.1 (1.0) A_{1g} [R]	465.2 (0) A_{2u}^2 [I]	469.0 (0) B_{2g}^1 [S]						
	1 TL	0 (0) A''_2 [I]	406.1 (1.0) A'_1 [R]	472.5 (0) A''_2 [I]									
	2 TL	0 (0) A_{2u} [I]	41.4 (0.46) A_{1g} [R]	405.5 (0) A_{2u} [I]	407.6 (1.0) A_{1g} [R]	470.2 (0) A_{2u} [I]	471.0 (0.001) A_{1g} [R]						
	3 TL	0 (0) A''_2 [I]	28.8 (0.55) A'_1 [R]	51.5 (0) A''_2 [I]	404.9 (0.003) A'_1 [R]	406.5 (0) A''_2 [I]	407.9 (1.0) A'_1 [R]	468.3 (0) A''_2 [I]	470.62 (0.001) A'_1 [R]	470.61 (0) A''_2 [I]			
	4 TL	0 (0) A_{2u} [I]	22.3 (0.53) A_{1g} [R]	41.5 (0) A_{2u} [I]	54.0 (0.02) A_{1g} [R]	404.6 (0) A_{2u} [I]	405.8 (0.01) A_{1g} [R]	407.1 (0) A_{2u} [I]	408.0 (1.0) A_{1g} [R]	467.9 (0) A_{2u} [I]	468.8 (0.0001) A_{1g} [R]	470.6 (0) A_{2u} [I]	470.8 (0.0003) A_{1g} [R]

Table 5-3 LDA calculated results for the Γ phonons in 1-4TL and bulk WSe₂. All the format is the same with in Table 5-2.

In-plane Modes	bulk	0 (0) E_{1u}^1 [I]	23.76 (0.47) E_{2g}^2 [R]	174.67 (0) E_{2u} [S]	176.31 (0) E_{1g} [R]	247.93 (1.0) E_{2g}^1 [R]	248.17 (0) E_{1u}^2 [I]						
	1 TL	0 (0) $E' [I+R]$	175.93 (0) $E'' [R]$	250.24 (1.0) $E' [I+R]$									
	2 TL	0 (0) E_u [I]	17.08 (0.4) E_g [R]	175.42 (0) E_u [I]	176.26 (0.012) E_g [R]	249.19 (1.0) E_g [R]	249.31 (0) E_u [I]						
	3 TL	0 (0) $E' [I+R]$	11.92 (0) $E'' [R]$	21.28 (0.46) $E' [I+R]$	175.17 (0) $E'' [R]$	175.84 (0.016) $E' [I+R]$	176.38 (0) $E'' [R]$	248.21 (1.0) $E' [I+R]$	249.18 (0) $E'' [R]$	249.20 (0.91) $E' [I+R]$			
	4 TL	0 (0) E_u [I]	9.51 (0.02) E_g [R]	17.26 (0) E_u [I]	22.72 (0.64) E_g [R]	175.03 (0) E_u [I]	175.52 (0.010) E_g [R]	176.06 (0) E_u [I]	176.40 (0.004) E_g [R]	248.11 (1.0) E_g [R]	248.23 (0) E_u [I]	249.20 (0.75) E_g [R]	249.19 (0) E_u [I]

Out-of-plane Modes	bulk	0 (0) A_{2u}^1 [I]	37.60 (0.0) B_{2g}^2 [S]	249.58 (0) B_{1u} [S]	252.27 (1.0, 0) A_{1g} [R]	307.66 (0) A_{2u}^2 [I]	309.91 (0) B_{2g}^1 [S]						
	1TL	0 (0) A''_{2u} [I]	251.32 (1.0) A'_1 [R]	312.55 (0) A''_{2u} [I]									
	2 TL	0 (0) A_{2u} [I]	27.01 (0.06) A_{1g} [R]	250.48 (0) A_{2u} [I]	251.77 (1.0) A_{1g} [R]	310.75 (0) A_{2u} [I]	311.26 (0.0001) A_{1g} [R]						
	3 TL	0 (0) A''_{2u} [I]	19.38 (0.07) A'_1 [R]	33.49 (0) A''_{2u} [I]	250.17 (0.02) A'_1 [R]	251.17 (0) A''_{2u} [I]	252.13 (1.0) A'_1 [R]	309.54 (0) A''_{2u} [I]	310.99 (0.0001) A'_1 [R]	310.96 (0) A''_{2u} [I]			
	4 TL	0 (0) A_{2u} [I]	14.56 (0.07) A_{1g} [R]	27.11 (0) A_{2u} [I]	35.58 (0.003) A_{1g} [R]	250.00 (0) A_{2u} [I]	250.72 (0.06) A_{1g} [R]	251.55 (0) A_{2u} [I]	252.22 (1.0) A_{1g} [R]	309.26 (0) A_{2u} [I]	309.87 (0.00001) A_{1g} [R]	310.91 (0) A_{2u} [I]	310.98 (0.0001) A_{1g} [R]

Among all the calculated phonon modes in 1-4TL and bulk MoS₂ and WSe₂ displayed in Table 5-2 and Table 5-3, the experimentally observed intralayer E_{2g}^1 and A_{1g} modes are highlighted in red. Note that the notations E_{2g}^1 and A_{1g} should be only applicable for bulk crystal, and the experimentally observed Raman peaks in 2D crystals should correspond to E' and A'_1 , respectively, for odd-TLs; and to E_g and A_{1g} , respectively, for even-TLs. However, for the convenience of discussion, the two high frequency intralayer vibrational modes in MX₂ 2D crystals are often referred to as E_{2g}^1 and A_{1g} in Raman spectroscopy, and this is also what we did in the previous sections. Note that the highlighted modes in NTL and bulk MoS₂ are the ones with the highest Raman intensity among their *suits*, and even among all the in-plane or out-of-plane phonon modes in crystal with given thickness, consistent with the fact that their corresponding Raman peaks are the strongest features in the Raman spectra. For a NTL 2D crystal with $N > 2$, there are more than one phonon mode with finite Raman intensity, as shown in Table 5-2 and Table 5-3. For example, both two E' modes with frequencies of 385.4 cm⁻¹ and 387.2 cm⁻¹, respectively, are supposed to be identified in a 3TL MoS₂, since LDA calculations predict close Raman intensities for them (1 and 0.76). Experimentally, however, we cannot resolve the two Raman peaks in the corresponding frequency region, probably due to the close frequencies of the two modes and a much larger Raman intensity difference in reality than the LDA calculated one. Nevertheless, we believe that it is fairly reasonable to assign the two experimentally observed high frequency Raman peaks as shown in Figure 5-1a and Figure 5-2a to the

phonon normal modes highlighted in red for bulk and few-TL MoS₂ and WSe₂, respectively.

Figure 5-7 Comparison between the experimental (with 532 nm excitation) and LDA calculated frequencies of the (a) E_{2g}^1 , (b) A_{1g} , and (c) $A_{1g} - E_{2g}^1$ in MoS₂ bulk and 2D crystals. The calculated results are down shifted with 3.1 cm⁻¹ and 1.3 cm⁻¹, respectively, to achieve an agreement with the experimental data at the bulk limit.

We next compare the calculated and experimental data on the frequency evolution trends of the intralayer E_{2g}^1 and A_{1g} modes in 1-9TL and bulk MoS₂, as shown in Figure 5-7. Overall, the LDA calculations (black solid squares in Figure 5-7a, b) overestimate the experimental Raman peaks frequencies (red and blue solid spheres in Figure 5-7a, b) by a few wavenumbers, which is still within the systematic error. To show a better comparison, we down shift the calculated data by ~3.1 cm⁻¹ for the E_{2g}^1 mode and ~1.3 cm⁻¹ for the A_{1g} mode (black open squares in Figure 5-7a, b) to align the calculated frequencies with the experimental ones at the bulk limit. Despite of slight quantitative discrepancy at the extreme 2D limit, the blueshift and redshift of the E_{2g}^1 and A_{1g} modes are perfectly captured by the LDA calculations, consistent with previous *ab initio* investigations.¹³¹ Moreover, the frequency difference between these two modes are also displayed in Figure 5-7c, where the pink spheres are the experimental data and the black solid squares are the LDA calculated results with discrepancies of only ~1 cm⁻¹ in the 2D limit (1-3TL) and ~2 cm⁻¹ in the 3D bulk limit. Figure 5-8 displays the both the calculated and experimental

data on the frequency evolution trends of the intralayer E_{2g}^1 and A_{1g} modes in 1-7TL and bulk WSe₂, where a small discrepancy of $\sim 1 \text{ cm}^{-1}$ has been achieved for both modes. Such a nice agreement between calculations and experiments indicate that the mechanisms that govern the anomalous lattice vibrations in MoS₂ and WSe₂ 2D crystals have been well captured by our LDA calculations.

Figure 5-8 Comparison between the experimental (with 633 nm excitation) and LDA calculated frequencies of the (a) E_{2g}^1 , (b) A_{1g} , and (c) $A_{1g} - E_{2g}^1$ in WSe₂ bulk and 2D crystals. The calculated data are shown as black solid squares and the experimental data are colored solid spheres.

5.3.3 Surface Effect Versus Thickness Effect-A Physical Picture

To understand the anomalous lattice vibrations better, we take one step further by analysing the inter-TL and intra-TL force constants up to the second nearest neighbors, which have been demonstrated sufficient to predict the anomalous Davydov splitting between the E_{1u}^2 and E_{2g}^1 modes in the bulk limit (Figure 5-6c). MoS₂ is used as an example for the discussion in this section.

Four force constants are taken into account to in the LDA calculations: the nearest neighbor Mo-S interactions within one TL (k_{Mo-S-1}), the second nearest neighbor S-S interactions within one TL (k_{S-S-2}), the nearest neighbor S-S interactions between two

adjacent TLs (k_{S-S-1}), and the second nearest neighbor Mo-S interactions between two adjacent TLs (k_{Mo-S-2}), as illustrated in Figure 5-6b.²²⁴ The spatial variation of the force constants in 1-6TL and bulk MoS₂ are shown in Figure 5-9, where the superscript S stands for the in-plane shear force constants and C represents the out-of-plane compressive ones. For a given NTL, the index of the interaction pairs are demonstrated by the schematic on the right in Figure 5-9, with the zero point being the center of the 1D atomic chain. Therefore, the atomic interaction pairs at the crystal surfaces have the largest indices. In general, the out-of-plane force constants are larger than the in-plane ones, in agreement with that fact that the out-of-plane phonons modes have larger frequencies than the in-plane ones, for a pair with the same displacement pattern, such as the B_{2g}^1 (469.0 cm⁻¹) and E_{2g}^1 (384.9 cm⁻¹) modes in bulk (Figure 5-6c).

Figure 5-9 Spatial variations of LDA calculated inter-atomic force constants in bulk and NTL MoS₂. The superscript ‘S’ or ‘C’ in the force constants represent in-plane and out-of-plane, respectively. The indices of interaction pairs are illustrated in the schematic atomic chain for NTL on the right, with the center of the chain being zero and the interaction pairs at the outmost towards the surfaces having the largest indices.

Among the four different force constants considered, the largest one is the Mo-S interaction within one TL k_{Mo-S-1} , which is around one order larger than the S-S interaction within one TL k_{S-S-2} , and two orders larger than the interactions between two TLs k_{S-S-1} and k_{Mo-S-2} . Remarkably, the force constants between the atomic pairs at the surface of the crystal are much different from those interior ones. For example, the strongest k_{Mo-S-1} at the surface is around 2.6% larger than in the one in the interior, which is consistent with previous report on a contraction of the spacing between the top S and Mo atomic planes of MoS₂ bulk crystal by a magnitude of around ~5% or less through a dynamical low energy electron diffraction method.²³³ Moreover, a clear difference between the out-of-plane force constants in bulk and the interior of the 2D crystals can be identified, which can be attributed to a decreased dielectric screening effect in 2D crystals along the out-of-plane direction with limited atomic stacks. In the in-plane direction, however, the long range coulomb interactions are not much affected in 2D crystals with maintained periodicity, and therefore the interior force constants are very close to those in bulk.

The decrease of the dielectric screening in 2D crystals is further confirmed by the self-interaction terms of the Mo and S atoms (Figure 5-10), which is defined as the diagonal elements of the dynamical matrix at the Brillouin zone center.^{131, 224} Similar with the spatial variations of the force constants displayed in Figure 5-9, both the Mo and S self-interaction terms are increased at the surface of a NTL 2D crystal. Moreover, while the in-plane self-interactions in the interior of the 2D crystals are almost the same as in the bulk, the out-of-plane ones are stronger than the bulk case. These results indicate that the decreased dielectric screening effect is mainly along the out-of-plane direction, and is negligible in-plane. Molina-Sánchez *et al.* have attributed the anomalous frequency evolutions of the E_{2g}^1 mode to a decrease of dielectric screening in 2D crystals,¹³¹ which, however, should not be the reason according to our results since the E_{2g}^1 mode only involves in-plane vibrations. Instead, we believe that the increased atomic interactions at the crystal surfaces, hereafter we refer it as the “surface effect”, should be the key factor to govern the anomalous lattice vibrations.

Figure 5-10 Spatial variations of the LDA calculated self-interaction terms of Mo and S atoms in 1-6TL and bulk MoS₂. The subscript x and z refer to the in-plane and out-of-plane components, respectively.

So far, we have demonstrated that both the spatial variations and the thickness dependence of the force constants, that is to say, the “surface effect” and “thickness effect”, respectively, need to be taken into account when discussing the frequency evolutions of a phonon mode in MoS₂ bulk and 2D crystals. To better distinguish surface effect from the thickness effect, we next in turn compute the frequencies of the E_{2g}^1 and A_{1g} modes in bulk and N TL crystals with and without surface relaxations, respectively. Four different models are considered: (1) rigid surfaces with the bulk force constants, (2) rigid surfaces with the interior force constants of the 2D crystals, (3) two relaxed surfaces with the surface force constants, and (4) one relaxed surface and one rigid surface. Note that all the force constants used in the above models are from the LDA calculations (Figure 5-8) and the computed frequency trends are shown in Figure 5-11a and b, respectively. The y axes correspond to the frequency difference with respect to the bulk $\Delta\omega = \omega(N\text{TL}) - \omega(\text{bulk})$. Without the surface effect, as in model 1 and 2, the E_{2g}^1 mode exhibits a red frequency shift with decreasing number of TLs, while the blueshift can be well predicted with the surface effect, as in model (3) and (4). This result provides solid evidence that the surface

effect is responsible for the anomalous frequency trend of this mode. The redshift of the A_{1g} mode with decreasing thickness can be captured by all the four models, as shown in Figure 5-11b. The redshifts according to model 1 and 2 suggest that they are the direct results of the thickness effect. Quantitatively, the redshift becomes less with the consideration of the surface relaxation (model 3 and 4), indicating that the surface effect counterbalances part of the thickness effect. Note that with surface relaxation only on one side (model 4), the frequency trends are right in between the models of two rigid surfaces (model 2) and two relaxed surfaces (model 4), further confirming the adverse influences of the surface and thickness effects on the frequency evolution trends. Moreover, the effect of the dielectric screening can also be reflected in the results given by model 1 and 2, where the thickness dependence of the dielectric screening is neglected in the former but included in the latter. The frequency of the out-of-plane mode A_{1g} in model 2 shows slight redshift respective to model 1, while the in-plane E_{2g}^1 modes are not affected at all, consistent with our analysis from the self-interactions in Figure 5-10.

By far, a simple physical picture with the competition between the thickness effect and the surface effect can be presented for the anomalous lattice vibrations in MoS₂ bulk and 2D crystals. The thickness effect causes red frequency shift of both E_{2g}^1 and A_{1g} modes from 3D to 2D, which can be intuitively understood as a result of decreased amount of interaction pairs. It is not hard to imagine that the out-of-plane A_{1g} mode is more sensitive to the crystal thickness with spatial confinement along its displacing direction, than the in-plane E_{2g}^1 mode, which is supported by the computation results of up to $\sim 9 \text{ cm}^{-1}$ of redshift of the A_{1g} mode in 1TL, compared with $\sim 0.6 \text{ cm}^{-1}$ redshift of the E_{2g}^1 mode with pure thickness effect in model 1 and 2. On the other hand, the surface effect would counteract with the thickness effect by increasing the phonon frequencies with increased force constants at the crystal surfaces. For the E_{2g}^1 mode, the surface effect overbalances the small red frequency shift caused by the thickness effect in 2D and achieve a net blueshift. The large thickness induced redshift of the A_{1g} mode, however, cannot be over taken by the surface effect and therefore remains redshift with a decreased magnitude. Overall, a net

blueshift in 1TL caused by the surface relaxation is estimated to be $\sim 5 \text{ cm}^{-1}$ for the E_{2g}^1 mode and $\sim 3.5 \text{ cm}^{-1}$ for the A_{1g} mode. The higher sensitivity to the surface effect of the E_{2g}^1 mode can be reflected by its vibrational schematics as displayed in Figure 5-11c, where the displacement amplitudes decrease rapidly towards the surfaces of the 2D crystals, while not as affected in the A_{1g} mode. Although the quantitative investigations of the intralayer frequency evolution trends have only been presented on MoS₂ in this section, we believe that the conclusion drawn here can be applied to MoSe₂, WS₂ and WSe₂ as well, since they share the same crystal structure and similar atomic interactions.

Figure 5-11 Force constant model computed frequency evolutions of the intralayer (a) A_{1g} and (b) E_{2g}^1 modes as a function of crystal thickness and their vibrational normal modes (c, d) in NTL and bulk MoS₂. The length of the arrow is proportional to the magnitude of the displacement.

5.4 Effect of Lower Dimensionality and Symmetry on Raman Spectra

5.4.1 Unexpected Raman Features in WSe₂ 2D Crystals

So far, all the bulk Raman-active modes that can be observed under our back scattering geometry, the E_{2g}^2 , E_{2g}^1 and A_{1g} modes have been investigated in MX₂ 2D crystals through Raman spectroscopy. Besides, unexpected Raman features that correspond to unobservable phonon modes can also be identified in the Raman spectra of some 2D crystals under certain circumstances. In this section, we demonstrate the Raman spectroscopy of the bulk E_{1g} and B_{2g}^1 modes in the WSe₂ and MoSe₂ 2D crystals. The former corresponds to a Raman-active mode that cannot be observed in the back scattering geometry (see section 2.4.2), and the latter corresponds to an optically inactive mode.

Figure 5-12 Raman spectra of supported 1-7TL and bulk WSe₂ under 532 nm excitation under (a) $\bar{z}(xx)z$ and (c) $\bar{z}(xy)z$ polarization configurations, respectively. (b) Zoom-in spectra of (a) in the range of 290 cm⁻¹ to 330 cm⁻¹. (d) Raman spectra of suspended 2-5TL WSe₂ under the $\bar{z}(xx)z$ polarization configuration.

Figure 5-12 displays the high frequency Raman spectra of 1-7TL and bulk WSe₂ with the excitation of a 532 nm laser line with polarization dependence. The Raman peak located around 250 cm⁻¹ correspond to the unresolved E_{2g}^1 and A_{1g} modes, and the broad Raman feature located around 260 cm⁻¹ is commonly assigned to a two-phonon scattering process

involving the LA phonon at the M point, as discussed in section 5.2. Note that the E_{2g}^1 and A_{1g} peaks can be well resolved under 633 nm excitation (see Figure 5-2). The excitation wavelength dependence of the spectra is probably due to the resonant Raman scattering effect. Beside these known Raman features, a peak located around 310 cm^{-1} can also be clearly identified in 2-7TL and bulk WSe_2 with a slight blue frequency shift ($<1\text{ cm}^{-1}$) from bulk to 2TL, as shown in Figure 5-12b. Moreover, this peak becomes largely suppressed under the $\bar{z}(xy)z$ polarization configuration (Figure 5-12c). To exclude the potential substrate effect, Raman spectroscopy has also been conducted on suspended few-TL samples (Figure 5-12d), where the peak still remains. To some extent, this new peak resembles the ultralow frequency S1 peak with the fact that it is only absent in 1TL. However, its high frequency nature can exclude its possibility of being an interlayer vibrational modes. The frequency of this peak, 310 cm^{-1} happens to identical to that of the optically inactive B_{2g}^1 mode, 309.9 cm^{-1} , according to our first principles calculations (see Table 5-3). We therefore tentatively assign this Raman peak to the B_{2g}^1 mode, as denoted in Figure 5-12b and d. The polarization dependence of this peak is also consistent with the out-of-plane vibrations of the B_{2g}^1 mode. This phonon mode assignment is in agreement with Tonndorf *et al.* in their previous Raman study.²¹³

Figure 5-13 Raman spectra of WSe_2 bulk and 2D crystals under 488 nm excitation with the few-TL samples (a, c) supported on SiO_2/Si substrates and (b, d) suspended. The Raman

peaks located at around 176 cm^{-1} (E_{1g}) and around 310 cm^{-1} (B_{2g}^1) are demonstrated by (a, b) and (c, d), respectively.

The Raman observation of the optically inactive B_{2g}^1 mode in the WSe₂ bulk crystal seems beyond comprehension. Interestingly, this Raman peak disappears in the bulk with 488 nm excitation while conserves in NTL ($N>1$), as shown in Figure 5-13c. Moreover, another weak Raman peak located around 176 cm^{-1} can also be identified in few-TLs, as shown in the pink shaded region of Figure 5-13a. Both the 176 cm^{-1} and 310 cm^{-1} peaks are also observed on suspended samples (Figure 5-12b and d). We tentatively assign the 176 cm^{-1} peak to the Raman-active E_{1g} mode with a frequency of $\sim 177.5 \text{ cm}^{-1}$ in the bulk.²¹⁸

Figure 5-14 Raman spectra of (a) bulk and (b) 2TL WSe₂ excited by lasers of different wavelengths under the $\bar{z}(xx)z$ polarization configuration. The Raman peaks located at around 176 cm^{-1} (E_{1g}) and around 310 cm^{-1} (B_{2g}^1) are denoted by the red asterisks.

The identification of both the E_{1g} and B_{2g}^1 modes through Raman spectroscopy seem highly sensitive to the crystal thickness as well as the excitation wavelength. We next investigate the Raman spectra of bulk and 2TL WSe₂ using difference laser lines with wavelengths from 457 nm to 785 nm, as shown in Figure 5-14. In bulk crystals, the E_{1g} peaks located around 176 cm^{-1} cannot be observed under any excitation wavelength,

consistent with the Raman symmetry selection rule. The B_{2g}^1 peak, however, can be observed in the Raman spectra under 532 nm and 514 nm excitations, as denoted by the red asterisks in Figure 5-14a. On the other hand, in 2TL, the E_{1g} peaks can be identified under 457 nm, 488 nm, and 502 nm excitations; the B_{2g}^1 peak can also be observed with similar intensity to that of the E_{1g} peak under 457 nm excitation, and with much stronger intensities under 488 nm, 502 nm, 514 nm and 532 nm excitations. The excitation wavelength dependence of the Raman spectra strongly suggest that resonant Raman scattering takes place in the frequency range we investigated, which might be able to account for the presence of the optically inactive B_{2g}^1 mode in bulk WSe₂ crystals under 514 nm and 532 nm excitations.

Figure 5-15 Thickness and excitation wavelength dependent Raman spectra of MoSe₂ 2D crystals in the range of 120 cm⁻¹ to 440 cm⁻¹. (a) Raman spectra of 1-5TL MoSe₂ under the $\bar{z}(xx)z$ polarization configuration with 488 nm excitation. (b) Raman spectra of 1-5TL MoSe₂ under the $\bar{z}(xy)z$ polarization configuration, with 488 nm excitation. (c) Raman spectra of 2TL MoSe₂ under the $\bar{z}(xx)z$ polarization configuration with various excitation wavelengths.

Both E_{1g} and B_{2g}^1 modes have also been observed in 1-5TL MoSe₂, located at around 170 cm⁻¹ and 350 cm⁻¹, respectively, as shown in Figure 5-15. No distinctive frequency

shift can be identified for both Raman peaks in different number of TLs. The strong Raman peaks located around 243 cm^{-1} correspond to the bulk A_{1g} mode, as discussed in section 5.2. Similar with in WSe₂, the B_{2g}^1 peak appears stronger than the E_{1g} peak under the $\bar{z}(xx)z$ polarization configuration with 488 nm excitation (Figure 5-15a). Under the perpendicular polarization configuration (Figure 5-15b), the B_{2g}^1 peak is largely suppressed while the E_{1g} peak can still be clearly identified, in agreement with the in-plane vibration manner of the E_{1g} mode. Moreover, both peaks are absent in the case of 1TL. An investigation on excitation wavelength dependence of the Raman spectra has also been conducted on 2TL MoSe₂ (Figure 5-15c), with varying laser lines from 457 nm to 633 nm, where the E_{1g} peak can only be observed under 488 nm excitation, while the B_{2g}^1 peak is present under 457-532 nm excitations. Preliminary Raman measurements with several excitation wavelengths have also been conducted on MoS₂ (532, 633, 671 nm) and WS₂ (457, 488, 502, 514, 532, 633 nm) 2D crystals without a clear identification of the E_{1g} and B_{2g}^1 modes in the expected frequency regime, probably due to their weak Raman intensities or inappropriate excitation laser lines.

5.4.2 Dimensionality Dependence of Phonon Symmetries

The experimental observation of the unexpected E_{1g} and B_{2g}^1 modes in WSe₂ and MoSe₂ 2D crystals can be understood from the phonon evolution rule from 1TL to bulk. As discussed in section 5.3.2, there exist six *suits* of phonon modes in any given *N*TL MX₂ 2D and bulk crystals. Each *suit* of phonon modes originate from one of the six intrinsic phonon modes in 1TL MX₂ (as shown in Figure 4-9a), and have very close frequencies while different optical activities due to different crystal symmetries of odd- and even-TLs.

The Raman-active E_{1g} mode of bulk MX₂ with its conjugate pair, an optically inactive E_{2u} mode, are evolved from a Raman-active E'' mode in 1TL. Meanwhile, the IR-active A_2'' mode of 1TL evolves into the optically inactive B_{2g}^1 and an IR-active A_{2u} modes in the

bulk, as demonstrated in Figure 4-9. The phonon evolution processes from 1TL to NTL and bulk, in terms of phonon frequencies and phonon symmetries, are reflected in Table 5-4 and Table 5-5 for the above two *suits* of phonon modes, respectively. Phonon frequencies and Raman intensities (I_{xx}) are calculated through LDA, as discussed in previous sections. The relative Raman intensities shown in the parenthesis are normalized by the largest value within each row.

Table 5-4 LDA calculated results for the phonon *suits* in 1-4TL and bulk WSe₂ that originate from the E'' mode of 1TL. All the format is the same with in Table 5-2. The phonon modes highlighted in red have the strongest Raman intensity among the row.

bulk	174.67 (0) E_{2u} [S]	176.31 (0) E_{1g} [R]		
1TL	175.93 (0) E'' [I]			
2TL	175.42 (0) E_u [I]	176.26 (1) E_g [R]		
3TL	175.17 (0) E'' [R]	175.84 (1) E' [I+R]	176.38 (0) E'' [R]	
4TL	175.03 (0) E_u [I]	175.52 (1) E_g [R]	176.06 (0) E_u [I]	176.40 (0.4) E_g [R]

Table 5-5 LDA calculated results for the phonon *suits* in 1-4TL and bulk WSe₂ that originate from the A_2'' mode of 1TL. All the format is the same with in Table 5-2. The phonon modes highlighted in red have the strongest Raman intensity among the row.

bulk	307.66 (0) A_{2u}^2 [I]	309.91 (0) B_{2g}^1 [S]		
1TL	312.55 (0) A_{2u}'' [I]			
2TL	310.75 (0) A_{2u} [I]	311.26 (1) A_{1g} [R]		

3TL	309.54 (0) A''_2 [I]	310.99 (1) A'_1 [R]	310.96 (0) A''_2 [I]	
4TL	309.26 (0) A_{2u} [I]	309.87 (0.01) A_{1g} [R]	310.91 (0) A_{2u} [I]	310.98 (1) A_{1g} [R]

Even though the E'' mode in 1TL is Raman-active, the computed Raman frequency is zero under the $\bar{z}(xx)z$ polarization configuration, which is similar with the Raman-active E_{1g} mode in the bulk. Recall the group theory analysis in section 4.3.2, where the Raman tensor of the E'' mode in odd-TLs has nonzero xz and yz components. Therefore, this mode cannot be probed in our back scattering geometry, consistent with absence of the E_{1g} peak in 1TL WSe₂ (Figure 5-13) and MoSe₂ (Figure 5-15). On the other hand, the Raman-active E_g modes in even-TLs and the Raman-active E' modes in odd-TLs both have nonzero xx and xy components in their Raman tensors, and therefore can experimentally probed by the back scattering Raman spectroscopy. Note that the phonon symmetries are different in odd-TLs, even-TLs and bulk, and the correct notations can be found in Table 5-4 and Table 5-5. While for the convenience of discussion, we still use E_{1g} to describe the experimentally observed Raman peaks in NTL, as shown in previous section. Similarly, the bulk notation B_{2g}^1 is used in NTL for the same reasoning. We tentatively believe that the experimentally observed E_{1g} and B_{2g}^1 peaks in WSe₂ and MoSe₂ 2D crystals correspond to the modes highlighted in red from Table 5-4 and Table 5-5, since they are predicted to possess the largest Raman intensities among their phonon *suits* in any give NTL. Moreover, the LDA predicted phonon frequencies exhibit very little TL number dependence, within a discrepancy of $<1 \text{ cm}^{-1}$ among 2-4TL, consistent with our experimental results shown in Figure 5-13 and Figure 5-15.

The vibrational normal modes of the E'' and A_2'' modes in 1TL MX₂ and the experimentally observed E_{1g} and B_{2g}^1 (highlighted in red in Table 5-4 and Table 5-5) modes in 2-4TL are displayed in Figure 5-16. Note that the displacement magnitudes of the atoms towards the surface are smaller than the interior ones, similar with the case of

the in-plane E_{2g}^1 mode (Figure 5-11c), as a result of the surface effect; while out-of-plane lattice vibrational mode are not as affected, as shown by the schematics of the B_{2g}^1 (Figure 5-16a) and A_{1g} (Figure 5-11d) modes.

Figure 5-16 Displacement schematics of the E'' and A_2'' modes in 1TL MX₂ and the modes highlighted in red from Table 5-5 and Table 5-5. The length of the arrow is proportional to the displacement magnitude of the atom.

Based on the above analysis, the experimentally observed Raman peaks in this section corresponding to unexpected bulk phonon modes have been uncovered and properly assigned to the correct lattice vibrations. The effect of lower crystal symmetry and dimensionality can be well reflected in the change of phonon properties from 2D to 3D, in terms of phonon quantity, phonon symmetry, as well as the phonon activity, all of which can be comprehensively explained according to the phonon evolution rule.

5.5 Summary

In conclusion, we have systematically investigated all the four *suits* of high frequency intralayer vibrational modes in MX_2 bulk and 2D crystals, commonly known as the E_{2g}^1 , A_{1g} , and E_{1g} , B_{2g}^1 mode using the bulk phonon notations. The E_{2g}^1 and A_{1g} modes exhibit distinct frequency shift from 3D to 2D in all the four MX_2 materials, which can be interpreted as a result of the competition between the surface effect and the thickness effect. The E_{1g} and B_{2g}^1 modes are Raman-forbidden in MX_2 bulk crystals with a back scattering geometry, however, become Raman-active in the few-TL cases, as a result of the lower crystal symmetry and dimensionality of the 2D crystals.

In addition to the two *suits* of low frequency interlayer vibrational modes (shear and breathing) investigated in Chapter 4, all the six *suits* of Γ phonon mode in MX_2 bulk and 2D crystals have been probed and well understood through a combination of Raman spectroscopy, first principles calculations and group theory analysis. Crystal symmetry and dimensionality play the key role in determining the phonon properties, in terms of phonon quantity, symmetry, and optical activity. Our results shed light on a general understanding of the phonon evolution from 3D to 2D in all the layered materials.

Chapter 6 Lattice Dynamics in Bi₂X₃ (X=Se, Te) 2D Crystals

6.1 Introduction

The phonon properties of the layered topological insulators Bi₂Se₃ and Bi₂Te₃ through Raman spectroscopy, especially in the extreme 2D regime, have not been investigated as extensively as in the transition metal dichalcogenides, limited by the nontrivial preparations of high-quality 2D crystals. So far, the most systematic thickness-dependent Raman spectroscopy on bismuth chalcogenide 2D crystals has been presented by Zhang *et al.*¹²⁸ and Wang *et al.*,¹³³ respectively, on few-QL Bi₂Se₃ nanoplatelets (down to 4QL) synthesized through a wet chemical method and few-QL Bi₂Te₃ thin films (down to 1QL) grown through the MBE method, in addition to some other scattered reports.^{161, 234, 235} All of the four intrinsic bulk phonon modes, two A_{1g} and two E_g modes, are also present in the Bi₂X₃ 2D crystals, with some frequency shifts and broadening of the Raman peaks from 3D to 2D, similar with our observations in the transition metal dichalcogenide systems as discussed in the previous two chapters. Some new Raman features have also been reported in the ultrathin Bi₂Te₃ thin films (<3QL), which were tentatively attributed to the surface phonon modes.¹³³ From the theoretical point of view, Cheng *et al.* compared the phonon properties of Bi₂Te₃/Bi₂Se₃ monolayer and bulk crystals through *ab initio* calculations, from which they predicted the phonon frequency change between bulk and 1QL. Besides, they also found that the spin-orbit coupling effect is important for the determination of the phonon frequencies.¹²⁹

Dimensionality and symmetry can largely influence the phonon properties in layered materials. From 3D to 2D, due to the change of the crystal symmetry, the intrinsic phonon properties, in terms of both phonon mode quantity and optical activity (Raman/IR activities), are completely different. In general, more phonon normal modes exist in 2D crystals, and while the Raman-active modes in bulk are also Raman-active in 2D, the reverse is not necessarily true.²³⁶ This dimensionality effect has been well reflected in the transition metal dichalcogenide 2D crystals by the Raman detection of new ultralow frequency interlayer as well as high frequency intralayer phonon modes, as discussed in Chapter 4 and 5, respectively. Although the high frequency intralayer phonons in Bi₂X₃

2D crystals have been extensively reported, the interlayer vibrational modes as predicted to be universal in all the layered materials, have yet been investigated in the topological insulator systems (Bi_2Te_3 , Bi_2Se_3 and Sb_2Te_3), either theoretically or experimentally.

In this chapter, we demonstrate the experimental probing of the interlayer vibrational modes in Bi_2Te_3 and Bi_2Se_3 2D crystals in the ultralow frequency region ($5\text{-}30\text{ cm}^{-1}$), combining Raman spectroscopy, first principles calculations and group theory analysis. The low frequency interlayer vibrational modes are strictly excluded in the 3D bulk, due to a higher crystal symmetry. Experimentally, we observe that both interlayer shear and breathing modes exhibit blueshifts with a decreasing thickness, which well agrees with the density functional theory (DFT) calculations and can be interpreted by a simple linear chain model. Besides, a substrate induced low frequency phonon mode has been identified in few-layer Bi_2Te_3 , which is tentatively believed to be originated from the interactions between the Bi_2Te_3 thin films and the substrates. In the high-frequency regime, Raman peaks corresponding to the bulk phonon normal modes are found to exhibit variations in frequency and linewidth in 2D crystals, which can be well understood by the 2D phonon confinement effect.

6.2 Phonon Properties in 3D and 2D Bi_2X_3

6.2.1 Irreducible Representations of Phonon Modes

Group theory analysis of the Γ phonon modes is the first step to understand the phonon properties in Bi_2X_3 bulk and 2D crystals. The crystalline structure of Bi_2X_3 has been shown in Figure 1-5a, where the bulk crystal has a rhombohedral structure and belongs to the space group $D_{3d}^5 (R\bar{3}m)$.¹²³ Since the atomic layers are arranged in a /ABC/ stacking manner, the rhombohedral primitive unit cell (black polyhedron in Figure 1-5a) overruns three QLs and contains five atoms, in accordance with the chemical formula.^{97, 125} Consequently, there are 15 Brillouin Zone center (Γ) phonon modes, three acoustic modes and twelve optical modes. The irreducible representations of the phonon modes can be written as $\Gamma_{\text{bulk}} = 3E_u + 3A_{2u} + 2E_g + 2A_{1g}$, among which $2E_g$ and $2A_{1g}$ are Raman-active,

$2E_u$ and $2A_{2u}$ are IR-active, and the rest three are acoustic phonon modes (E_u and A_{2u}). The two-fold degenerate E symmetry modes represent in-plane (shear) vibrations while the non-degenerate A symmetry modes vibrate out-of-plane (breathing) along the c axis. The lattice displacements of all the Raman-active and IR-active phonon modes in the bulk are displayed in Figure 1-7b. Note that an equivalent hexagonal unit cell including only one QL is used for displaying the vibrational normal modes instead of the complex rhombohedral unit cell overrunning three QLs, for the convenience of demonstration, which is also a common practice in those complex structures.^{96, 123, 125} For the two-fold degenerate in-plane E modes, only the lattice vibrations within the paper surface are presented in Figure 1-7b, and the unshown ones are displacing with the same manners while perpendicularly to the paper surface.

In the case of Bi_2X_3 2D crystals with finite number of QLs, the symmetry is lowered in comparison to that of its bulk counterpart due to the lack of the translation symmetry along the c axis. Symmetry analysis indicates that few-QL Bi_2Te_3 has a hexagonal structure which belongs to the space group D_{3d}^3 ($P\bar{3}m1$). The primitive unit cell of a N QL (N is the number of QLs) system consists of $5N$ atoms and therefore $15N$ Γ phonon modes, among which there are $15N-3$ optical phonon modes. The irreducible representations of the zone center phonons can be written as:

$$\Gamma_{\text{odd}} = \frac{5N-1}{2}(A_{1g} + E_g) + \frac{5N+1}{2}(A_{2u} + E_u), \quad N = 1, 3, 5, \dots \text{ for odd-QL systems, and}$$

$$\Gamma_{\text{even}} = \frac{5N}{2}(A_{1g} + A_{2u} + E_g + E_u), \quad N = 2, 4, 6, \dots \text{ for even-QL systems.}$$

Since the inversion symmetry is kept in few-QL Bi_2X_3 , all their Γ phonon modes are exclusively Raman-active (E_g and A_{1g}) or IR-active (E_u and A_{2u}). The Raman tensors of the E_g and A_{1g} modes in 2D crystals have the same forms as in the bulk as follows:

$$A_{1g} : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

$$E_g : \begin{pmatrix} c & d & 0 \\ d & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & c \\ d & c & 0 \end{pmatrix}.$$

Consequently, in our back scattering geometry of Raman measurements, both E_g and A_{1g} modes can be observed under the $\bar{z}(xx)z$ configuration, while only the E_g mode is observable under the $\bar{z}(xy)z$ configuration due to its nonzero off-diagonal Raman tensor components, as predicted by the symmetry selection rule (section 2.4.2).

6.2.2 Phonon Evolution Rule from 2D to 3D

Although the quantity of Γ phonon modes of bulk and few-QL Bi_2X_3 varies from 3D to 2D with a QL number dependence, the phonon symmetries keep the same. The main reason is that although the space group symmetry of the 2D crystal is lowered in comparison with that of the 3D bulk, they still possess the same point group symmetry D_{3d} , which determines the irreducible representations of the phonon modes. This is much different from the case of transition metal dichalcogenides, where the odd-TLs, eve-TLs and bulk all belong to different point groups, which result in completely different phonon symmetries.

The quantity and behavior of the phonon modes in 2D and 3D Bi_2X_3 can be well understood by the phonon evolution rule: each of the 15 normal modes in 1QL will evolve into N modes in $N\text{QL}$, keeping the vibration manner the same within each QL while alternating the relative displacement phases among different QLs. The N modes that share the same origin come with very close frequencies and we refer them a *suit*, as discussed in section 5.3.2. A *suit* of modes could have different Raman/IR activities, depending on their vibration symmetries. Following the evolution rule, $N\text{QL}$ (space group D_{3d}^3 ($P\bar{3}m1$)) has $15N$ phonon modes (15 *suits*), and consequently the bulk crystal with infinite QLs should

have infinite number of modes, which however, are reduced to a finite amount (15) in their irreducible representations due to a higher crystal symmetry (space group $D_{3d}^5 (R\bar{3}m)$). Following the evolution rule, the in-plane acoustic mode in 1QL will evolve into $N-1$ interlayer shear modes (E_g and E_u) in NQL , and the out-of-plane acoustic mode evolves into $N-1$ breathing modes (A_{1g} and A_{2u}), with each layer displacing as a unit and the vdW force being the only restoring force. In the bulk Bi_2X_3 , inter-QL vibrational modes are strictly excluded in the irreducible Γ phonon representations with its rhombohedral crystal structure. The absence of the interlayer modes in bulk Bi_2X_3 distinguishes the topological insulator system from other layered materials such as graphene, MoS_2 , WSe_2 , *etc.*, where one of the intrinsic bulk phonon modes corresponds to an interlayer shear mode (E_{2g}^2).^{220,}

237

In summary, the reduced crystal symmetry of Bi_2X_3 2D crystals compared to the 3D bulk gives rise to the interlayer vibrational phonon modes in NQL ($N>1$). Interestingly, 1QL and bulk Bi_2X_3 happen to share exactly the same phonon properties, that is to say, the same quantity (15) and same symmetries, where the interlayer shear and breathing modes are absent.

6.3 Polarized Raman Spectroscopy

Polarized Raman measurements were conducted on few-QL Bi_2Te_3 (down to 2QL) nanoplates grown on both SiO_2/Si and mica substrates, as well as few-QL Bi_2Se_3 (down to 1QL) nanoplates grown on mica substrates through vapor transport, as introduced in chapter 3. A 633 nm laser line was used as the excitation with a power of less than 0.05 mW on the sample to avoid heating.

Typical Stokes and anti-Stokes Raman spectra of 3QL Bi_2Te_3 and 3QL Bi_2Se_3 were displayed in Figure 6-1 under both $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations. Note that Bi_2Te_3 nanoplates on SiO_2/Si and mica substrates give essentially the same Raman spectra with slight difference in the low frequency region, which will be discussed in detail in later sections. Here, the Raman spectra shown in Figure 6-1a and b are from the as-

grown 3QL Bi₂Te₃ nanoplates on SiO₂/Si substrates. The four intrinsic Raman-active phonon modes of bulk crystals (E_g^1 , A_{1g}^1 , E_g^2 and A_{1g}^2) are identified as the four major Raman peaks in the high frequency region (25~160 cm⁻¹) for Bi₂Te₃, and in the range of 25~210 cm⁻¹ for Bi₂Se₃, as shown in Figure 6-1b and d, respectively. The phonon mode assignment is based on the peak frequencies reported in previous studies.^{97, 123, 127, 128, 133} Note that a given phonon mode has higher frequency in Bi₂Se₃ than in Bi₂Te₃, due to the smaller molecular weight of the former. The assignment of the four modes is further verified by their polarization dependence, where the out-of-plane A_{1g}^1 and A_{1g}^2 peaks are largely suppressed under the $\bar{z}(xy)z$ configuration while the in-plane E_g^1 and E_g^2 modes still remain, consistent with the symmetry analysis above. Besides the four Raman-active modes, an additional Raman peak located around 69 cm⁻¹ (denoted by the black asterisk) was also observed in 3QL Bi₂Te₃ at the higher-frequency side of the A_{1g}^1 peak under both parallel and perpendicular polarizations, indicating that it might correspond to an in-plane vibrational mode, like the E_g modes. Similar new Raman features have also been reported in MBE grown Bi₂Te₃ ultrathin films,¹³³ and the exact normal mode assignment is unclear yet.

In the ultralow frequency range (5~30 cm⁻¹), three sharp Raman peaks are observed for the first time in Bi₂Te₃ (Figure 6-1a), with comparable intensities to those of the high-frequency peaks. In the same frequency range, two intense peaks are also present in 3QL Bi₂Se₃ (Figure 6-1c). The ultralow frequency characteristics of these peaks naturally relate them with the interlayer vibrational modes, as a result of the weak vdW restoring force. The polarization dependence of these Raman peaks indicate that they likely correspond to the out-of-plane breathing modes (labeled as B), and in-plane shear mode (labeled as S), respectively. Recall that the phonon evolution rule predicts $N-1$ interlayer shear and $N-1$ breathing mode in N QL Bi₂X₃, as discussed in section 6.2.2. Our results show evidence for the Raman detection of these interlayer vibrational modes. Note that all the Raman-active modes in few-QL and bulk Bi₂X₃ have either E_g or A_{1g} symmetries, and therefore the interlayer breathing (B) and shear (S) modes here should correspond to the A_{1g} and E_g vibrational modes, respectively.

Figure 6-1 Stokes and anti-Stokes Raman spectra of (a, b) 3QL Bi₂Te₃ and (c, d) 3QL Bi₂Se₃ both $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarization configurations in the high frequency region (25-160 cm⁻¹) and low frequency region (5-30 cm⁻¹), respectively.

6.4 Ultralow Frequency Interlayer Vibrational Modes in Bi₂X₃ 2D Crystals

6.4.1 Thickness-Dependent Raman Spectroscopy

To further investigate the ultralow frequency Raman peaks, thickness-dependent Raman measurements were conducted on 2-11QL Bi₂Te₃ on SiO₂/Si substrates, as well as on 1-7QL Bi₂Se₃ on mica substrates. Figure 6-2 shows the Raman spectrum evolution with varying thickness under $\bar{z}(xx)z$ (a) and $\bar{z}(xy)z$ (b) polarization configurations. The Raman peak located at around 35 cm⁻¹ in Bi₂Te₃ and 37 cm⁻¹ in Bi₂Se₃ corresponds to the

bulk E_g^1 mode, as denoted by the pink dashed lines. Although the E_g^1 peak can be clearly seen in all the Bi_2Se_3 samples, it can only be clearly identified in 2QL Bi_2Te_3 . Many low frequency Raman peaks were observed in few-QL Bi_2Te_3 and Bi_2Se_3 , whose frequencies are extracted from the spectra and listed in Table 6-1 and Table 6-2. Their low frequency nature indicates that they likely correspond to the interlayer shear and breathing modes, depending on their polarization dependence. Among all the Raman features in the range of $5\sim 30\text{ cm}^{-1}$, two trends of peaks in particular stand out, both showing blueshifts with decreasing thickness, as guided by the blue and red dashed lines. Above 8QL Bi_2Te_3 and 6QL Bi_2Se_3 , the two peaks get submerged in the Rayleigh scattering background and are beyond the detection limit. Moreover, these two trends of peaks exhibit different polarization dependence and we therefore refer them as B1 (breathing) and S1 (shear), as denoted, for the convenience of discussion.

Figure 6-2 Low frequency Raman spectrum evolutions as a function of QL number in Bi_2Te_3 and Bi_2Se_3 . (a, b) Low frequency Raman spectra of 2-11QL and bulk Bi_2Te_3

measured using the (a) $\bar{z}(xx)z$ polarization configuration, and (b) the $\bar{z}(xy)z$ polarization configurations. (c-d) Low frequency Raman spectra of 1-7QL Bi_2Se_3 measured using the (c) $\bar{z}(xx)z$ polarization configuration, and (d) the $\bar{z}(xy)z$ polarization configurations. The evolutions of the S1, B1 and I peaks are guided using red, blue and black dashed lines, respectively. The intralayer vibrational mode E_g^1 barely shifts in Bi_2Se_3 2D crystals with different QLs, as indicated by the pink dashed line in (c) and (d). In few-QL Bi_2Te_3 , the E_g^1 mode can be distinctively observed only in 2QL.

Table 6-1 Frequencies of the interlayer vibrational modes in 2-12QL Bi_2Te_3 extracted from Figure 6-2a. The B1 and S1 modes are highlighted in blue and red, respectively. Other breathing and shear modes are determined by their polarization dependence and yet assigned to any specific vibrational modes.

$\text{cm}^{-1} \backslash \text{QL}$	2	3	4	5	6	7	8	10	11
Acoustic	12.9	10.4	8.3						
B1		21.3	16.1	13.3	11.6	10.0	8.8		
Other breathing modes				27.3	23.3	20.1	17.3	24.9	18.9
						24.9	25.7		20.5
						28.9			
S1		12.5	9.6	7.2	6.4	5.6	4.8		
Other shear modes				15.3	13.7	8.8	10.4	6.8	
						14.5	12.5	12.9	

Table 6-2 Frequencies of the interlayer vibrational modes in 2-7QL Bi_2Se_3 extracted from Figure 6-2c. The lowest-frequency breathing and shear modes are highlighted in blue and red, respectively. Other breathing and shear modes are determined by their polarization dependence and yet assigned to any specific vibrational modes.

$\text{cm}^{-1} \backslash \text{QL}$	2	3	4	5	6	7
B1	20.7	13.5	10.2	8.6	6.8	
			27.5	15.9	20.0	17.1

Other breathing modes				28.3	28.7	
S1	12.7	9.4	7.4	5.8		
Other shear modes					12.5	11.2

The frequencies of the B1 and S1 peaks show very high sensitivity to the nanoplate thickness. In Bi_2Te_3 , the B1 peak blueshifts by $\sim 21 \text{ cm}^{-1}$ from 8QL (8.8 cm^{-1}) to 2QL (30.0 cm^{-1}), and the S1 peak blueshifts by $\sim 13 \text{ cm}^{-1}$ from 8QL (4.8 cm^{-1}) to 2QL (18.0 cm^{-1}); in Bi_2Se_3 , the B1 peak blueshifts by $\sim 14 \text{ cm}^{-1}$ from 6QL (6.8 cm^{-1}) to 2QL (20.7 cm^{-1}), while the S1 peak blueshifts by $\sim 7 \text{ cm}^{-1}$ from 5QL (5.8 cm^{-1}) to 2QL (12.7 cm^{-1}). Therefore, low frequency Raman spectroscopy provides a fast and convenient approach to the thickness determination of Bi_2Te_3 and Bi_2Se_3 2D crystals. Note that the B1 and S1 peaks are very weak in 2QL Bi_2Te_3 , while still can be identified through a careful Lorentzian fitting and lineshape analysis.

Figure 6-3 Demonstration of the B1 and S1 peaks in 2QL Bi_2Te_3 . (a-b) Low frequency Raman spectra as-grown 2QL Bi_2Te_3 nanoplates on (a) SiO_2/Si and (b) mica substrates under the $\bar{z}(xx)\bar{z}$ (black spectra) and $\bar{z}(xy)\bar{z}$ (blue spectra) polarization configurations. The red lines are the multi-Lorentzian fitted results.

Figure 6-3 shows the polarized Raman spectra of 2QL Bi_2Te_3 on SiO_2/Si and mica substrates, respectively, in the frequency range of $5\sim 80 \text{ cm}^{-1}$. The out-of-plane interface

mode (I), lowest-frequency breathing mode (B1) and the A_{1g}^1 mode are largely suppressed under the $\bar{z}(xy)z$ configuration, while the in-plane E_g^1 mode is conserved. From the Lorentzian fitting, the B1 mode with frequency of $\sim 30 \text{ cm}^{-1}$ can be clearly identified for both samples. We tentatively assign the S1 mode to the weak peak located at 18.0 cm^{-1} under the $\bar{z}(xy)z$ configuration in 2QL Bi_2Te_3 on mica substrates, which however, cannot be well resolved under the $\bar{z}(xx)z$ configuration since it is likely merged into the tail of the much stronger I peak (15.2 cm^{-1}) and the uprising Rayleigh background. The S1 mode cannot be identified in 2QL Bi_2Te_3 on SiO_2/Si substrates (Figure 6-3a), probably due to its extreme weak Raman intensity in this case. In the limit of bulk, no low frequency Raman peaks can be observed at all, in accordance with the group theory analysis that the interlayer vibrational modes do not exist in bulk Bi_2X_3 . Raman peaks with frequencies even smaller than that of the S1 peak are identified in 2-4QL Bi_2Te_3 , also showing blueshift with decreasing thickness, as guided by the black dashed lines. We tentatively attribute these peaks to an interface mode (labelled as I) resulted from the interaction between the nanoplate and the substrates, which will be discussed later.

6.4.2 First Principles Calculations

First principles calculations of Γ phonon modes of 1-5QL and bulk $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Se}_3$ are performed within the DFT as implemented in the plane-wave pseudopotential code QUANTUM-ESPRESSO²⁰¹. The LDA²⁰² to the exchange-correlation functional is employed in the norm-conserving²⁰³ pseudopotential throughout the calculation. The spin-orbit coupling effect is included self-consistently by using fully relativistic pseudopotentials for the valence electrons. To get converged results, plane-wave kinetic energy cutoffs of 50 Ry and 500 Ry are used for the wave functions and charge density, respectively. The slabs are separated by 16 Å of vacuum to prevent interactions between slabs (this value has been tested for convergence of phonon frequencies). A Monkhorst-Pack k -point mesh of $13 \times 13 \times 13$ and $13 \times 13 \times 1$ are used to sample the Brillouin Zones for the bulk and thin films systems, respectively. In the self-consistent calculation, the convergence threshold for energy is set to 10^{-9} eV . All the atomic coordinates and lattice

constants are optimized with the Broyden–Fletcher–Goldfarb–Shanno quasi-Newton algorithm. During the structure optimization, the symmetry of hexagonal is imposed on *NQL*. The structures are considered as relaxed when the maximum component of the Hellmann-Feynman force acting on each ion is less than 0.003 eV/Å. Non-resonant Raman intensities of the Γ phonon modes are calculated within the Placzek approximation²²⁹, as discussed in section 4.4.3. Since both all the Raman-active phonon modes in Bi_2X_3 bulk and 2D crystals can be observed under the $\bar{z}(xx)z$ polarization configuration, their Raman intensities under this configuration (I_{xx}) are computed in this chapter to show consistency with experiments.

Our calculations confirm the existence of interlayer vibrational modes with ultralow frequencies ($<40 \text{ cm}^{-1}$) in few-QL Bi_2Te_3 and Bi_2Se_3 , as expected according to the phonon evolution rule. In a *NQL* system, there are $N-1$ two-fold degenerate interlayer shear modes (E_g) and $N-1$ non-degenerate interlayer breathing modes (A_{1g}) with different frequencies. Note that no interlayer vibrational modes exist in 1QL since there is no interlayer vdW restoring force, in good agreement with our experimental observations in 1QL Bi_2Se_3 . The calculated phonon mode symmetries and Raman/IR activities are presented in Table 6-3 and Table 6-4 for 2-5QL Bi_2Te_3 and Bi_2Se_3 , respectively. In general, interlayer shear modes with the lowest, third lowest, or more generally the j^{th} (j is odd number) lowest frequencies are Raman-active (E_g), while the rest are IR-active (E_u). Similarly, interlayer breathing modes with the j^{th} (j is an odd number) lowest frequencies are Raman-active (A_{1g}), while the rest are IR-active (A_{2u}). Non-resonant Raman intensity calculations indicate that lowest frequency breathing (shear) modes carry the largest Raman intensities (I_{xx}) under the $\bar{z}(xx)z$ polarization configuration, among all the Raman-active interlayer breathing (shear) modes, as shown by the relative Raman intensities in the parentheses for each normal mode. Therefore, it is reasonable to assign our experimentally observed B1 and S1 Raman peaks to the lowest frequency shear and breathing modes, respectively.

Table 6-3 DFT calculated frequencies of the interlayer breathing and shear modes in 2-5QL Bi_2Te_3 . In each *NQL*, the breathing (shear) modes are listed from low frequency to high frequency, from left to right. The modes highlighted in red are Raman-active and the

ones in black are IR-active. The phonon mode symmetries are indicated above each column. The calculated Raman intensities (I_{xx}) are normalized by the largest value of the interlayer shear or breathing modes in a given NTL and are shown in the parentheses.

thickness \ cm^{-1}	Interlayer breathing modes				Interlayer shear modes			
	A_{1g}	A_{2u}	A_{1g}	A_{2u}	E_g	E_u	E_g	E_u
2QL	23.50 (1)				13.90 (1)			
3QL	16.82 (1)	29.82 (0)			9.70 (1)	18.02 (0)		
4QL	11.43 (1)	23.21 (0)	33.11 (0.16)		7.80 (1)	14.34 (0)	19.09 (0.015)	
5QL	9.64 (1)	18.71 (0)	27.89 (0.31)	34.47 (0)	5.35 (1)	12.37 (0)	16.38 (0.011)	20.03 (0)

Table 6-4 DFT calculated frequencies of the interlayer breathing and shear modes in 2-5QL Bi_2Se_3 . The modes highlighted in red are Raman-active and the ones in black are IR-active. The format is the same as in Table 6-3.

thickness \ cm^{-1}	Interlayer breathing modes				Interlayer shear modes			
	A_{1g}	A_{2u}	A_{1g}	A_{2u}	E_g	E_u	E_g	E_u
2QL	22.03 (1)				14.99 (1)			
3QL	16.12 (1)	29.69 (0)			11.05 (1)	16.91 (0)		
4QL	11.21 (1)	21.48 (0)	32.07 (0.007)		7.85 (1)	15.87 (0)	19.05 (0.01)	
5QL	8.49 (1)	18.69 (0)	26.53 (0.07)	32.48 (0)	7.24 (1)	12.81 (0)	16.14 (0.05)	19.26 (0)

Note that the Raman intensities for the interlayer vibrational modes in the few-QL Bi_2X_3 system are different from in the few-TL MX_2 system as discussed in section 4.4.3, where largest Raman intensities are possessed by the highest frequency shear modes and the

lowest frequency breathing modes, respectively. It is the Raman intensity that determines the experimental observation of the any given interlayer breathing (shear) modes among the $N-1$ ones in a N -layer 2D crystal, and consequently the frequency evolution trends of the corresponding Raman peaks. For instance, the frequency of the highest frequency breathing (shear) mode follows a redshift with decreasing crystal thickness, while that of the lowest frequency one follows a blueshift, which is consistent with our experimental observations in both the transition metal and bismuth chalcogenide layered materials.

Figure 6-4 Normal mode displacements for all the interlayer shear and breathing modes in 2-5QL Bi_2X_3 . The normal modes are arranged from low to high frequency, from left to right. The Raman/IR activity is listed below the displacement and the ones highlighted in red (the highest frequency) correspond to the S1 and B1 modes that are observed experimentally, respectively. For the interlayer shear modes, all the Raman-active modes

have E_g symmetry and all the IR-active modes have E_u symmetry. For the interlayer breathing modes, all the Raman-active modes have A_{1g} symmetry and all the IR-active modes have A_{2u} symmetry.

The normal mode displacements of all the interlayer vibrational modes in 2-5QL Bi_2X_3 are shown in Figure 6-4, where the displacements of the QLs are directed by the arrows with lengths proportional to the vibration magnitudes. The experimentally observed S1 and B1 modes are highlighted in red and have very similar vibration patterns: all the N QLs are divided into two parts that are vibrating out-of-phase against each other; while the QLs within each part are vibrating in-phase. Note that more out-of-phase displacements among the QLs correspond to larger restoring forces and consequently higher frequencies, as demonstrated by the normal modes in Figure 6-4.

6.4.3 Linear Chain Model

A comparison between the experimental data and DFT calculated results are shown in Figure 6-5. Figure 6-5a plots out the frequencies of the S1 (red solid squares) and B1 (blue solid circles) peaks in 2-8QL Bi_2Te_3 extracted from Figure 6-2a, as well as the calculated frequencies of the lowest frequency shear modes (red open squares) and the lowest frequency breathing modes (blue open circles) in 2-5QL Bi_2Te_3 . Similarly, the frequencies of the S1, B1 peaks extracted from Figure 6-2c, and the calculated results in 2-5QL Bi_2Se_3 are shown in Figure 6-5b. The experimental frequency evolution trends with varying thickness are well predicted by calculations for both the B1 and S1 modes. For 2-5QL Bi_2Te_3 , the calculations overall underestimate the experimental values by an average of $\sim 4.8 \text{ cm}^{-1}$ for the B1 mode and $\sim 2.9 \text{ cm}^{-1}$ for the S1 mode; while in 2-5QL Bi_2Se_3 , the calculated results overestimate the experiments by an average of $\sim 1.2 \text{ cm}^{-1}$ for the B1 mode and $\sim 1.5 \text{ cm}^{-1}$ for the S1 mode.

Figure 6-5 Frequency evolutions versus QL number for the measured and calculated interlayer breathing and shear modes in few-QL Bi_2Te_3 and Bi_2Se_3 , as well as and the linear chain model interpretation. (a-b) Plot of the lowest frequency shear (S1) and breathing (B1) mode frequencies as a function of QL number in few-QL (a) Bi_2Te_3 and (b) Bi_2Se_3 extracted from Figure 6-2. The red solid (dashed) line is the fitting of the experimental (calculated) S1 modes versus thickness using the linear chain model. The blue solid (dashed) line is the fitting for the B1 modes using the same formula as for the S1 modes. (c) Schematics of the linear chain model. The blue spheres represent QLs bonded by a nearest neighbor force constant K .

Beside the B1 and S1 modes, other experimentally observed minor low frequency peaks (mostly in 4QL and above) listed in Table 6-1 and Table 6-2 also correspond to some interlayer vibrational modes of higher frequencies, with vibration symmetries of either A_{1g} or E_g , depending on their polarization dependence in the Raman spectra. However, the exact normal mode assignment for these Raman peaks is not clear yet due to the considerable discrepancies between experiments and calculations.

The frequency evolutions of the S1 and B1 modes with varying thickness can be well understood by a simple linear chain model as used in Chapter 4, whose schematic is shown in Figure 6-5c, where the blue spheres represent single QLs bonded by the vdW force with a force constant K . In this model, it is assumed that the interactions between the substrates and Bi_2X_3 nanoplates are negligible, and only the ones between the nearest neighbor QLs

are significant. This simple linear chain model has been adopted to interpret the frequency evolutions of the interlayer vibrational modes in transition metal dichalcogenides (see section 4.5), as well as in few-layer graphene.²³⁷ Solving the linear chain model, the frequencies (in cm^{-1}) of the eigenmodes can be obtained as

$$\omega_{\alpha} = \sqrt{\frac{K}{2\mu\pi^2c^2} \left(1 - \cos\left(\frac{(\alpha-1)\pi}{N}\right) \right)}, \quad (6-1)$$

where $\alpha = 1$ mode corresponds to the acoustic phonon mode and $\alpha = 2, \dots, N$ corresponds to the breathing modes ($K = K_z$) and shear modes ($K = K_x$). μ is the mass per unit area of one Bi_2X_3 QL ($\mu=8.2\times10^{-6} \text{ kg/m}^2$ for Bi_2Te_3 ; $\mu=7.5\times10^{-6} \text{ kg/m}^2$ for Bi_2Se_3) and c is the light velocity in the unit of cm/s . For the lowest frequency interlayer breathing (B1) and shear (S1) modes, the aforementioned expression with $\alpha = 2$ fits both the measured and computed results very well for both Bi_2Te_3 and Bi_2Se_3 (see the fitted solid and dashed lines in Figure 6-5a, b). The good fitting indicates that the interface interactions between Bi_2X_3 QLs and the substrates, if there is any, do not affect much the frequency evolution of the interlayer vibrational modes with varying thickness. The in-plane and out-of-plane force constants for both Bi_2Te_3 and Bi_2Se_3 can be obtained from fitting the experimental and DFT calculated data, as shown in Table 6-5. Overall, the DFT calculations underestimate the experimental force constants by a factor of ~ 1.7 for Bi_2Te_3 , while overestimate that by a factor of ~ 1.3 for Bi_2Se_3 . Both experiments and calculations suggest that the out-of-plane force constants (K_z) are larger than the in-plane ones (K_x), by a factor of ~ 2.9 for Bi_2Te_3 and ~ 2.2 for Bi_2Se_3 , consistent with other layered systems like MoS_2 , WS_2 and WSe_2 , where K_z were found to be about 3 times as large as K_x , as shown in Table 4-8 (section 4.5).

Table 6-5 Force constants per unit area derived from fits to both experiments and LDA calculations in few-QL Bi_2Te_3 and Bi_2Se_3 according to the linear chain model.

		DFT (LDA)	Experiment
Bi_2Te_3	$K_z(10^{19} \text{ Nm}^{-3})$	8.21	13.33
	$K_x(10^{19} \text{ Nm}^{-3})$	2.76	4.57
Bi_2Se_3	$K_z(10^{19} \text{ Nm}^{-3})$	6.34	5.26

	$K_x(10^{19} \text{ Nm}^{-3})$	3.10	2.27
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6.4.3 Substrate Effect

Besides the lowest frequency breathing (B1) and shear (S1) modes, a Raman peak with even lower frequency has been identified in 2-4QL Bi_2Te_3 , as shown in Figure 6-2a. We tentatively assign this peak to an interface mode that results from the interaction between Bi_2Te_3 nanoplates and the substrates, since it exhibits substrate dependence. Figure 6-6 shows the low frequency Raman spectra in 2-4QL Bi_2Te_3 on SiO_2/Si and mica substrates, respectively. The spectra are carefully analyzed through multi-Lorentzian fitting on top of a polynomial background. While the B1 and S1 peaks barely show any substrate dependence, the I peak is very sensitive to the choice of substrates, implying its origin of a substrate introduced interface mode. Also note that the full-range Raman spectra are essentially the same for Bi_2Te_3 2D crystals on SiO_2/Si and mica substrates, except the different I peaks in 2-4QL. In 2-3QL, a higher frequency of the I mode is found on the mica substrates than SiO_2/Si . In 4QL, the I mode gets very close to the S1 mode on SiO_2/Si , while can barely be distinguished on mica. The high sensitivity of the interface mode to choices of substrates indicates different interaction strengths at different sample-substrate interfaces.

We model the effects of the interaction between Bi_2Te_3 nanoplates and the substrates by using a non-zero substrate-introduced force (force constant K_i) in the linear chain model with a substrate, whose schematic is shown in Figure 6-7a. This nonzero K_i results in eigenmodes that are different from those of the free linear chain model ($K_i=0$). Most distinctly, the zero-frequency acoustic mode corresponding to the eigenmode with $\alpha = 1$ becomes an interface mode (I) with finite frequency due to the presence of a restoring force. In order to understand how the interface force constants affect the observed frequencies, we fix the interlayer force constants to those derived for the free linear chain model fitting of the DFT calculated data (see Table 6-5), and vary the ratio between K_i and the interlayer force constant K . As shown in Figure 6-6d, e and f, for all values of K_i/K from 0 to 3, the frequency of the interface mode I is smaller than the S1 and B1 frequencies in 2-4QL

Bi_2Te_3 . Furthermore, for $K_i/K < 1$, the frequency of the interface mode I is significantly more sensitive to the value of K_i/K compared to the interlayer modes S1 and B1. Therefore, the experimental observations of the low frequency peak I in few-QL Bi_2Te_3 is consistent with the presence of an interaction between Bi_2Te_3 and the substrates. Moreover, the high sensitivity of the I peak frequency to the choice of substrates (Figure 6-6a, b, c) indicates that the substrate-induced interaction is likely to be weaker than the interlayer interaction within our as grown Bi_2Te_3 nanoplates, while still considerable to give rise to the interface mode. In the as grown few-QL Bi_2Se_3 nanoplates on mica, as well as the mechanical exfoliated multilayer graphene, MX_2 (M=Mo, W; X=S, Se) on SiO_2/Si substrates, the substrate-induced interaction is likely to be negligible since the low frequency mode I has not yet been observed.^{220, 237} The origin of this larger substrate-induced interaction for Bi_2Te_3 is unclear and requires further investigations.

Figure 6-6 Substrate-dependent Raman spectra and force constant modeling of the interface mode. (a-c) Low frequency Raman spectra of 2-4QL Bi_2Te_3 nanoplates grown on mica (blue dotted line) and SiO_2/Si substrates (red dotted line). The black solid lines are fitted results through the multi-Lorentzian fitting, and the green lines are the Lorentzian peaks

involved. The frequencies of the S1 and B1 modes do not show a substrate dependence, while that of the interface mode largely depends on the substrates. (d-f) Calculated frequencies of the B1, S1 and I modes of 2-4QL Bi_2Te_3 on a substrate with the ratio of the interface and interlayer force constants K_i/K varying from 0 to 3.

Figure 6-7 Interpretation of the S1, B1 and interface (I) mode frequencies through the linear chain model with a substrate. (a) Schematics of the linear chain on a substrate. K represents the nearest neighbor force constant between adjacent QLs, and the K_i is the interface force constant between the Bi_2Te_3 nanoplate and the substrates. (b) Comparison between the experimental and the calculated frequencies for the S1, B1 and the I modes through the linear chain model with a substrate with $K_i/K=0.5$. (c-d) Displacement schematics of the I, S1 and B1 modes in 2QL under the (c) free linear chain model and (d) linear chain model on a substrate. The arrows indicate the vibration directions of each QL and the lengths are proportional to the displacement amplitudes.

As an illustration, we plot the eigenmode frequencies from the linear chain model with a substrate with $K_i/K = 0.5$ in Figure 6-7b. The blueshift of the interface mode I and interlayer B1, S1 mode with decreasing thickness are maintained with the presence of the

substrate. The substrate effect on the frequencies of eigenmodes of the linear chain model can also be reflected in the normal mode displacements. Figure 6-7c, d display the vibrational schematics of the Interface mode (I), interlayer B1 and S1 modes in 2QL Bi₂Te₃ with and without a substrate, respectively. Compared to the free linear chain model (Figure 6-7c), the substrate plays its role by slightly changing the relative displacement magnitudes of the QLs while keeping the overall vibration patterns, which consequently causes the change of phonon mode frequencies.

6.5 High Frequency Intralayer Vibrational Modes in Bi₂X₃ 2D Crystals

6.5.1 Frequency and Linewidth Evolutions

We next discuss the high frequency intralayer phonon behaviors from 3D to 2D Bi₂Xe₃. Figure 6-8a and Figure 6-9a show the Stokes and anti-Stokes Raman spectra in the high frequency region (30~210 cm⁻¹) measured from 2-11QL and bulk Bi₂Te₃, as well as 1-7QL and bulk Bi₂Se₃, respectively. The four intrinsic Raman-active modes of bulk are observed around 36 cm⁻¹ (E_g^1), 62 cm⁻¹ (A_{1g}^1), 102 cm⁻¹ (E_g^2), 133 cm⁻¹ (A_{1g}^2) for Bi₂Te₃, and around 38 cm⁻¹ (E_g^1), 71 cm⁻¹ (A_{1g}^1), 131 cm⁻¹ (E_g^2), 173 cm⁻¹ (A_{1g}^2) for Bi₂Se₃, as denoted in the figures. The larger frequencies of all the modes in Bi₂Se₃ than in Bi₂Te₃ is due to the smaller molecular weight of the former. Note that the E_g^1 peak is very weak in Bi₂Te₃ but gets much pronounced when the thickness is decreased to 2QL, in contrast to the distinct E_g^1 peak in the MBE grown Bi₂Te₃ thin films.¹³³ In 2QL Bi₂Se₃ and above, all the four modes can be clearly identified from the Raman spectra; while in 1QL, only the E_g^1 peak can be well resolved in both Stokes and anti-Stokes spectra, with the presence of a weak hump located at 195 cm⁻¹.

Figure 6-8 Raman spectra of few-QL Bi₂Te₃ and analysis. (a) High frequency Stokes and anti-Stokes Raman spectra of bulk Bi₂Te₃ and 2-11QL nanoplates on SiO₂/Si substrates. (b-c) Zoom-in view of the (b) A_{1g}^1 and (c) A_{1g}^2 peaks with varying thicknesses. (d) A_{1g}^1 mode frequency vs. nanoplate thickness. The red solid circles are experimental data and the blue solid squares are the calculated results. The calculated data are down shifted by 5.9 cm⁻¹ (blue open squares) to match the experimental bulk frequency. (e) A_{1g}^2 mode frequency vs. nanoplate thickness. The pink solid circles are experimental data and the blue solid squares are the calculated results. The calculated data are up shifted by 2.6 cm⁻¹ (blue open squares) to match the experimental bulk frequency. (f) FWHM vs. thickness of both A_{1g}^1 and A_{1g}^2 modes, and the phenomenological fittings.

From 3D bulk to 2D crystals, some of the Raman peaks exhibit distinct frequency and linewidth changes. Most distinctively, the A_{1g}^1 peak shows a redshift of ~8 cm⁻¹ from bulk

to 2QL Bi₂Te₃, and a redshift of $\sim 5 \text{ cm}^{-1}$ from bulk to 2QL Bi₂Se₃, as shown in the zoom-in spectra (Figure 6-8b and Figure 6-9b). Meanwhile, the other out-of-plane A_{1g}^2 peak blueshifts by a magnitude of $\sim 6 \text{ cm}^{-1}$ in Bi₂Te₃ (Figure 6-8c), while the blueshift of this peak is not as distinct in Bi₂Te₃ (Figure 6-9c). In comparison, the peak positions of the two in-plane E modes (E_g^1 and E_g^2) do not show as strong QL number dependence, except for the slight redshift from 3QL to 2QL Bi₂X₃. The stronger dependence of the out-of-plane mode frequencies on the nanoplate thickness than that of the in-plane ones is consistent with our observations in the low frequency region as discussed in section 6.4, as well as previous Raman reports.^{128, 133} in other layered materials such transition metal dichalcogenides (Chapter 4 and 5).

Figure 6-9 Raman spectra of few-QL Bi₂Se₃ and analysis. (a) High frequency Stokes and anti-Stokes Raman spectra of bulk Bi₂Te₃ and 2-7QL nanoplates on SiO₂/Si substrates. (b-c) Zoom-in view of the (b) A_{1g}^1 and (c) A_{1g}^2 peaks with varying thicknesses. (d) A_{1g}^1 mode

frequency vs. nanoplate thickness. The red solid circles are experimental data and the blue solid squares are the calculated results. The calculated data are down shifted by 5.9 cm^{-1} (blue open squares) to match the experimental bulk frequency. (e) A_{1g}^2 mode frequency vs. nanoplate thickness. The pink solid circles are experimental data and the blue solid squares are the calculated results. (f) FWHM vs. thickness of both A_{1g}^1 and A_{1g}^2 modes, and the phenomenological fittings.

To quantitatively describe the Raman peak shifting and broadening from 3D to 2D Bi_2X_3 , careful lineshape analyses were conducted for the Raman spectra. Lorentzian fitting was well achieved for the A_{1g}^1 peak in Bi_2Te_3 (Figure 6-8b), as well as for the A_{1g}^2 peak in both Bi_2Te_3 and Bi_2Se_3 (Figure 6-8c, Figure 6-9c), where the fitted results are shown by the black solid lines and original spectra are represented by the colored solid lines. The A_{1g}^1 peaks of Bi_2Se_3 , however, exhibit distinct asymmetry with the right shoulders of the peaks arising. Such asymmetry has been well captured by the BWF lineshape as introduced in section 2.3.1,¹³⁵ and has been investigated by Zhang *et al.* in wet chemistry synthesized Bi_2Se_3 nanoplates.¹²⁸ The BWF Raman lineshape originates from the quantum interference between a discrete phonon state and a continuum of electronic or multiphonon states. The constructive or destructive interferences at different frequencies result in the frequency and lineshape renormalization of a Lorentzian Raman peak.^{135, 238} So far, the BWF lineshape has been observed in many systems such as doped Si crystals and Si nanowires,^{239, 240} carbon nanotubes,²⁴¹ graphene,²³⁷ *etc.*, and can be described by equation (2-9).

We fit the A_{1g}^1 peak of bulk and 2-7QL Bi_2Se_3 using equation (2-9), as shown by the black solid lines in Figure 6-9b. A clear demonstration of the good BWF fitting is shown in Figure 6-10a and b for 2QL and 7QL, respectively. The uprising right shoulder of the peaks indicate that constructive interference takes places at higher energy side of the A_{1g}^1 mode frequency while destructive interference occurs at its lower energy side. Moreover, it is worth noting that the asymmetry of the peak is more distinct in thinner nanoplates, as shown by the clear contrast between 2QL (Figure 6-10a) and 7QL (Figure 6-10b). The crystal thickness dependence of the asymmetry is shown in Figure 6-10c, where the

electron phonon coupling strength $1/q$ monotonically increases as decreasing number of QLs. The detailed information on the continuum states that are coupling with the A_{1g}^1 mode and the thickness dependent coupling strength are unclear yet and require further investigations. Similar evidences of the strong electron phonon interactions in Bi_2Se_3 have also been found through other investigation methods such as IR reflection and transmission,^{242, 243} ARPES,²⁴⁴ helium-atom scattering,²⁴⁵ as well as the electron transport measurements.²⁴⁶

Figure 6-10 BWF lineshape analysis of the A_{1g}^1 peak in 2-7QL and bulk Bi_2Se_3 . (a, b) BWF fitting in (a) 2QL and (b) 7QL Bi_2Se_3 . (c) The asymmetric parameter $1/q$ vs. crystal thickness.

The fitted frequencies and FWHMs of the A_{1g}^1 and A_{1g}^2 peaks are plot out as a function of QL number for bulk and few-QL Bi_2Te_3 (Figure 6-8d, e) and Bi_2Se_3 (Figure 6-9d, e), respectively. The frequency evolution of the A_{1g}^1 and A_{1g}^2 peaks from 3D to 2D Bi_2X_3 originates from the phonon confinement effect, as discussed in section 2.6, and can be numerically predicted by DFT calculations. The calculated frequencies of the A_{1g}^1 and A_{1g}^2 modes in 2-5QL Bi_2Te_3 and Bi_2Se_3 are shown in Figure 6-8d, e and Figure 6-9d, e, respectively, as the blue solid squares, with the fitted experimental results presented by the red and pink solid spheres. Overall, the calculations overestimate the experimental frequency of the A_{1g}^1 mode in both Bi_2Te_3 and Bi_2Se_3 , with discrepancies of 5.9 cm^{-1} and

3.8 cm⁻¹, respectively, in the bulk limit, which are still within the systematic error bar.²²⁴ On the other hand, the calculated results underestimate the A_{1g}^2 frequencies in bulk and few-QL Bi₂Te₃ by a magnitude of around 3 cm⁻¹, while the discrepancies between experiments and calculations vary in different thicknesses of Bi₂Se₃. The calculated frequency evolution trends, blueshift of the A_{1g}^1 mode and redshift of the A_{1g}^2 mode with decreasing thickness, overall agree well with the experiments, except the significant overestimation of the experimental blueshift of the Bi₂Se₃ A_{1g}^2 mode. A clearer demonstration can be made by systematically shifting the calculated data to achieve perfect agreement between the experiments and calculations in the bulk limit, as shown by the blue open squares in Figure 6-8d, e and Figure 6-9d. The broadening of the A_{1g}^1 and A_{1g}^2 peaks with decreasing thickness well follows the phenomenological exponential relationship $\Gamma_0(d) = A + B \exp(-d/C)$, where d represents the thickness of the Bi₂Te₃ nanoplates, and A, B, C are fitting parameters.^{128, 247} Good fitting was achieved in Bi₂Te₃ with A=2.4±0.08, B=33.9±7.9, C=1.1±0.1 for A_{1g}^1 , and A=7.6±0.03, B=46.0±7.4, C=0.9±0.05 for A_{1g}^2 , as shown by the blue solid lines in Figure 6-8f; in Bi₂Se₃ (Figure 6-9f), these fitted parameters are A=3.0±0.02, B=61.4±4.2, C=0.74±0.02 for A_{1g}^1 , and A=9.1±0.15, B=18.5±4.2, C=1.3±0.2 for A_{1g}^2 . The broadening of a Raman peak corresponds to a decreased phonon lifetime, and this phonon confinement effect gets more dominant when the sample size gets closer to the extreme 2D limit.

6.5.2 First Principles Calculations

The details of the first principles calculations for the Γ intralayer phonon modes of 1-5QL and bulk Bi₂Te₃/Bi₂Se₃ are the same as for the interlayer vibrational modes, as discussed in section 6.4.2.

Following the phonon evolution rule in section 6.2.2, the A_{1g}^1 and A_{1g}^2 modes in 1QL will respectively evolve into N modes in N QL. For the convenience of discussion, we refer the N modes with close frequencies as the A_{1g}^1 *suit* and A_{1g}^2 *suit*, respectively. Table 6-6

lists the calculated phonon mode frequencies, symmetries, as well as the Raman intensities (I_{xx}) under the $\bar{z}(xx)z$ polarization configuration, for the A_{1g}^1 *suit* in 1-5QL and bulk Bi_2Te_3 . Similar results for 1-5QL and bulk Bi_2Se_3 are shown in Table 6-7. Phonon modes with the j^{th} (j is odd) highest frequency among the *suit* are Raman-active with A_{1g} symmetry, and the rest ones are IR-active with A_{2u} symmetry. Moreover, the mode with the highest frequency among its *suit* in *NQL* carries the largest Raman intensity, as highlighted in red, which are likely corresponding to the experimentally observed A_{1g}^1 peaks. The red highlighted frequencies have been plotted out in Figure 6-8d and Figure 6-9d as the blue solid squares, where good quantitative agreements have been achieved with the experimental data. Therefore, we can draw the conclusion that the experimentally observed A_{1g}^1 peak in any *NQL* corresponds to the phonon mode with the highest frequency among its *suit*.

Table 6-6 DFT calculated results for the out-of-plane intralayer A_{1g}^1 *suits* in 1-5QL and bulk Bi_2Te_3 . In each *NQL*, the modes are listed from low frequency to high frequency, from left to right. The phonon frequencies (cm^{-1}) and relative Raman intensities I_{xx} (in parentheses) are listed in the first and second row, respectively, in each cell. The Raman intensity I_{xx} is normalized by the largest value in each row. The irreducible representations of the phonon modes are listed as the third row of each cell. All A_{1g} modes are Raman-active and all A_{2u} modes are IR-active. The modes highlighted in red are the experimentally observed ones.

Bulk	67.8 (1) A_{1g}				
1QL	55.0 (1) A_{1g}				
2QL	54.5 (0) A_{2u}	63.5 (1) A_{1g}			
3QL	54.1 (0.05) A_{1g}	59.6 (0) A_{2u}	65.6 (1) A_{1g}		

4QL	53.5 (0) A_{2u}	62.3 (0.03) A_{Ig}	65.0 (0) A_{2u}	66.7 (1) A_{Ig}	
5QL	53.4 (0.02) A_{Ig}	56.1 (0) A_{2u}	60.8 (0.02) A_{Ig}	63.6 (0) A_{2u}	66.9 (1) A_{Ig}

Table 6-7 DFT calculated results for the out-of-plane intralayer A_{1g}^1 suits in 1-5QL and bulk Bi_2Se_3 . All the format are the same as in Table 6-6.

bulk	75.7 (1) A_{Ig}				
1QL	67.8 (1) A_{Ig}				
2QL	65.0 (0) A_{2u}	70.9 (1) A_{Ig}			
3QL	65.0 (0.05) A_{Ig}	68.4 (0) A_{2u}	73.7 (1) A_{Ig}		
4QL	65.1 (0) A_{2u}	70.3 (0.03) A_{Ig}	72.0 (0) A_{2u}	74.6 (1) A_{Ig}	
5QL	65.2 (0.02) A_{Ig}	65.6 (0) A_{2u}	69.7 (0.02) A_{Ig}	72.3 (0) A_{2u}	74.5 (1) A_{Ig}

Table 6-8 DFT calculated results for the out-of-plane intralayer A_{2u} and A_{1g}^2 suits in 1-5QL and bulk Bi_2Te_3 . All the format are the same as in Table 6-6.

bulk	120.5 (0) A_{2u}	131.9 (1) A_{Ig}							
1QL	143.0 (0) A_{2u}	146.2 (1) A_{Ig}							
2QL	136.7 (0) A_{2u}	137.8 (1) A_{Ig}	142.3 (0.13) A_{Ig}	142.7 (0) A_{2u}					
3QL	128.9 (0) A_{2u}	135.4 (1) A_{Ig}	137.1 (0) A_{2u}	137.2 (0.07) A_{Ig}	141.2 (0.06) A_{Ig}	141.6 (0) A_{2u}			

4QL	124.4 (0) A_{2u}	133.3 (1) A_{1g}	135.1 (0.03) A_{1g}	135.8 (0.13) A_{1g}	136.8 (0.003) A_{1g}	137.4 (0) A_{2u}	140.9 (0) A_{2u}	141.1 (0) A_{2u}		
5QL	122.6 (0) A_{2u}	131.6 (1) A_{1g}	134.0 (0) A_{2u}	136.0 (0.25) A_{1g}	143.0 (0) A_{2u}	136.1 (0.05) A_{1g}	136.5 (0) A_{2u}	137.2 (0) A_{2u}	140.6 (0) A_{2u}	140.7 (0.005) A_{1g}

Table 6-9 DFT calculated results for the out-of-plane intralayer A_{2u} and A_{1g}^2 *suits* in 1-5QL and bulk Bi₂Se₃. All the format are the same as in Table 6-6.

bulk	163.2 (0) A_{2u}	174.6 (1) A_{1g}								
1QL	179.0 (0) A_{2u}	184.3 (1) A_{1g}								
2QL	165.1 (0) A_{2u}	176.8 (1) A_{1g}	178.9 (0) A_{1g}	179.8 (0.13) A_{2u}						
3QL	164.4 (0) A_{2u}	175.0 (1) A_{1g}	176.2 (0.7) A_{2u}	176.8 (0) A_{1g}	178.6 (0) A_{1g}	179.1 (0.12) A_{2u}				
4QL	162.6 (0) A_{2u}	173.9 (1) A_{1g}	175.3 (0) A_{1g}	175.9 (0.08) A_{1g}	176.6 (0.61) A_{1g}	177.1 (0) A_{2u}	178.9 (0.09) A_{2u}	182.3 (0) A_{2u}		
5QL	162.6 (0) A_{2u}	172.9 (1) A_{1g}	174.2 (0) A_{2u}	175.2 (0.16) A_{1g}	175.7 (0) A_{2u}	175.8 (0.59) A_{1g}	175.9 (0) A_{2u}	176.8 (0.38) A_{2u}	177.9 (0) A_{2u}	178.0 (0.001) A_{1g}

DFT calculations indicate show that the experimentally observed A_{1g}^2 peaks in Bi₂X₃ do not necessarily belong to the same phonon *suits* in different *NQL* cases. For 1QL and bulk Bi₂X₃, the A_{1g}^2 Raman peak does correspond to the only phonon mode of its *suit*, the Raman-active A_{1g}^2 mode; while in *NQL* ($N>1$), the Raman peaks shown in Figure 6-8c and Figure 6-9c in fact correspond to the phonon modes that evolve from an IR-active A_{2u} mode in 1QL, which is also the mode with the second highest frequency among all the 15 phonon modes. Table 6-8 and 6-9 display both the A_{2u} and A_{1g}^2 *suits* in 1-5QL and bulk Bi₂Te₃ and Bi₂Se₃. In 1QL, these two modes have very close frequencies, apart by $\sim 3 \text{ cm}^{-1}$ in Bi₂Te₃ and $\sim 5 \text{ cm}^{-1}$ in Bi₂Se₃; in *NQL* ($N>1$), these two *suits* of modes might have some frequency overlaps. Interestingly, non-resonant Raman intensity calculations indicate that

the largest Raman intensity among these two *suits* of phonon modes is possessed by the second lowest frequency mode, as highlighted in red in Table 6-8 and Table 6-9. We tentatively believe that the highlighted modes should correspond to the experimentally observed Raman peaks, which is confirmed by the good agreement for Bi₂Te₃ (Figure 6-8e). In Bi₂Se₃, despite of the lack of a good quantitative agreement between the Raman results and calculations for this mode (Figure 6-9e), the experimentally observed slight blueshift of the A_{1g}^2 Raman peak from 3D to 2D is captured by our phonon mode assignment.

6.6 Summary

In this chapter, the phonon properties in bulk and 2D Bi₂Te₃ and Bi₂Se₃ have been systematically investigated, through the combination of Raman spectroscopy, first principles calculations and group theory analysis. Crystal dimensionality plays a key role in determining the quantity and vibration symmetry of the phonon modes. The low frequency interlayer breathing and shear modes have been uncovered for the first time in the Bi₂X₃ 2D crystals, which however, are excluded in the 3D bulk due to the symmetry change. The frequency evolution of the interlayer vibrational modes with varying crystal thickness can be well interpreted by a linear chain model, which functions as an effective probe of the interlayer vdW force. An ultralow frequency interface mode has been identified in 2D Bi₂Te₃, which we tentatively propose to be originated from the substrate-crystal interface interactions. The thickness dependence of the high frequency Raman spectra reveals the phonon confinement effect in the 2D limit, which can also be well predicted by the DFT calculations. Our results brought into light a full picture of the phonon properties and their dependency on the crystal symmetry and dimensionality in the layered bismuth chalcogenide topological insulator materials.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

In this thesis, the phonon properties of the layered metal chalcogenides 2D crystals have been systematically investigated through Raman spectroscopy, supported by group theory analysis and first principles calculations. This thesis contains two main parts: preparation and characterizations of the 2D crystals for the transition metal dichalcogenides (MoS_2 , MoSe_2 , WS_2 , WSe_2) and bismuth chalcogenides (Bi_2Se_3 , Bi_2Te_3), as well as the phonon studies on these two families of materials.

High-quality mono- and few-TL transition metal dichalcogenide 2D crystals have been prepared on SiO_2/Si substrates through the well-established mechanical exfoliation method from their bulk crystals. Bi_2Te_3 nanoplates with thicknesses down to 2QL and large planar sizes (several to tens of microns) have been synthesized through the vapor transport method on both SiO_2/Si and mica substrates. Similarly, Bi_2Se_3 down to 1QL were synthesized using the same method on mica substrates. Both the transition metal dichalcogenide and bismuth chalcogenide 2D crystals exhibit high optical contrast on top of the Si substrates when capped with an optimal thickness of SiO_2 layer, which provides a fast and convenient method for the location and thickness determination of the 2D crystals. The vapor transport growth mechanism for the Bi_2Te_3 nanoplates has been comprehensively investigated and a Te-seeded growth model was revealed, where crystalline Te seeds firstly form thermodynamically and then initiate the epitaxial growth of the Bi_2Te_3 nanoplates. Similar growth mechanism might be expected for other bismuth chalcogenide layered materials. Moreover, electron transport measurements on the as-grown few-QL Bi_2Te_3 nanoplates revealed the weak anti-localization effect, which is resulted from the strong spin-orbit coupling in this topological insulator material.

A full picture of the intrinsic phonon normal modes of a crystal can be provided by the group theory analysis, according to which, the phonon properties, in terms of the phonon mode quantity, symmetry, and optical activity, are directly governed by the crystal symmetry and dimensionality. In general, more phonon normal modes exist in 2D crystals than in the 3D bulk, and when a Raman-active phonon mode in 3D should also be Raman-

active in 2D, the reverse is not necessarily true. The variation of the Γ phonon properties from 2D to 3D can be well guided by a general phonon evolution for all the vdW layered materials from monolayer to few-layers and eventually to bulk crystals. These theoretical predictions have been well demonstrated by Raman spectroscopy in both the ultralow frequency regime ($<50 \text{ cm}^{-1}$) for the interlayer vibrational modes, as well as the in high frequency regime ($>50 \text{ cm}^{-1}$) for the intralayer vibrational modes.

The presence of new interlayer vibrational modes in 2D crystals compared to in the 3D bulk is a solid evidence of the lowered crystal symmetry and dimensionality effect. In any layered 2D crystal composed of N vdW layers, these exist $N-1$ two-fold degenerate interlayer shear modes, and $N-1$ non-degenerate interlayer breathing modes. In the transition metal dichalcogenide 2D crystals, two shear and two breathing modes have been uncovered through ultralow frequency Raman spectroscopy. While the two interlayer shear modes in few-TLs correspond to a similar Raman-active shear mode in the bulk, the two Raman-active interlayer breathing modes in the 2D crystals correspond to an optically inactive mode in the 3D bulk. In bismuth chalcogenides, both the Raman-active interlayer breathing and shear modes of the hexagonal 2D crystals are strictly excluded in the 3D bulk, due to its higher rhombohedral symmetry. The frequency evolution trends (redshift or blueshift) of the Raman observed interlayer modes with varying crystal thicknesses, is simply governed by the phonon evolution rule, and can be quantitatively interpreted through a simple linear chain model.

The lowered symmetry and dimensionality effect of 2D crystals can also be reflected in the phonon property change of the intralayer vibrational modes from 3D to 2D. In the transition metal dichalcogenides, the high frequency intralayer B_{2g}^1 and E_{1g} modes transit from the Raman-forbidden to Raman-allowed symmetries under the $\bar{z}(xx)z$ polarization configuration from the 3D bulk to few-TLs, and then become Raman-forbidden again in the limit of 1TL, as have been experimentally demonstrated in WSe_2 and WS_2 . Anomalous lattice vibrations, commonly known as the blueshift of the E_{2g}^1 mode and redshift of the A_{1g} mode with decreasing number of TLs, have been observed through Raman spectroscopy in all the four transition metal dichalcogenide materials. What governs this phenomenon is the competition between the surface effect and the thickness effect, where

the former causes an upshift of the phonon mode frequency in thinner crystals, while the latter results in an opposite trend. For the bismuth chalcogenides, the high frequency intralayer modes exhibit similar frequency shifts from 3D to 2D, which can be well predicted by the first principles calculations. Besides the frequency changes, the Raman peaks generally experience broadening from 3D to 2D, indicating a decrease of the phonon lifetime, which can be attributed to the phonon confinement effect.

Overall, our results in this thesis shed light on a general understanding of the intrinsic phonon properties of the vdW layered materials and their evolutions from 2D to 3D. Most distinctively, the lower symmetry and dimensionality induced ultralow frequency interlayer vibrational modes are expected to be present in all the vdW layered 2D crystals.

7.2 Future Work

(1) Resonant Raman scattering in transition metal dichalcogenide 2D crystals

Resonant Raman scattering can be easily achieved in the transition metal dichalcogenides with excitation wavelengths in the visible to near-IR range, since the energies of the A and B excitons at the K point happen to fall in this frequency range. Under the resonant conditions, unexpected Raman features might appear corresponding to the multi-phonon scattering processes; meanwhile, some intrinsic phonon modes that are present under off resonance conditions might become absent on resonance. For example, as discussed in section 5.4.1, the intralayer B_{2g}^1 and E_{1g} modes can only be observed under the excitations of certain laser lines. Therefore, the analysis of resonant Raman spectra could be complicated, but essentially important for a comprehensive understanding of the phonon properties, as well as the electron phonon interactions.

Preliminary results show that Raman spectra of the transition metal dichalcogenides largely depend on the excitation wavelengths. Figure 7-1 displays the Raman spectra of 2TL WS₂ with excitation wavelengths varying from 457 nm to 633 nm. In the ultralow frequency regime ($<50\text{ cm}^{-1}$), the interlayer shear (S1) and breathing (B1) can be clearly identified under 457 nm, 488 nm and 502 nm, while evolve into completely different

Raman features with excitations from 514 nm to 633 nm. Similarly, in the high frequency regime, the broad Raman peak attributed to a two LA phonon scattering process (shaded in pink) gets more and more prominent with increasing excitation wavelength and finally overshadows the E_{2g}^1 peak under 514 nm, 532 nm and 633 nm excitations.

Figure 7-1 Raman spectra of 2TL WS_2 in the (a) ultralow frequency regime and (b) high frequency regime excited by lasers of various wavelengths under the $\bar{z}(xx)z$ polarization configuration.

Figure 7-2 Raman spectra of 1-6TL and bulk WS_2 excited by lasers with wavelengths of (a) 457 nm, (b) 532 nm and (c) 633 nm under the $\bar{z}(xx)z$ polarization configuration.

According to both the ultralow and high frequency Raman spectra, 457 nm excitation is an off resonance condition, while 532 nm and 633 nm excitations both are on resonance. Note that 532 nm and 633 nm happen to be close to the B and A exciton energies, respectively, of WS₂ 2D and bulk crystals. Thickness-dependent ultralow frequency Raman spectra under these three excitation wavelengths are shown in Figure 7-2. Under 532 nm, the lowest frequency interlayer shear mode (S1) can still be identified as shown by the red dashed line, but not for the interlayer breathing modes (B1, B2). Moreover, a broad Raman peak with thickness independence are present in both 1-7TL and bulk crystals, as guided by the blue dashed line in Figure 7-2b. Under 633 nm excitation, no interlayer vibrational modes can be identified at all, while a new broad Raman peak with thickness dependence are observed, as guided by the blue dashed line in Figure 7-2c. We tentatively attribute these new Raman features to electron related scattering (ERS), since they cannot be assigned to any known phonon scattering processes. Similar resonant Raman scattering phenomena have also been observe in WSe₂, and MoS₂.

A better understanding of the resonant Raman scattering in transition metal dichalcogenides requires systematic Raman spectroscopy on all the four materials with thickness, polarization, temperature, as well as excitation wavelength dependence. Furthermore, to investigate the potential electron related scattering in the ultralow frequency regime, Raman measurements should be conducted while tuning the charge carrier concentration in these materials, through chemical doping, or the gate of a FET device. More sophisticated techniques such as Raman spectroscopy in a magnetic field will also help shed light on the understanding of the electronic Raman scattering.

(2) Lasing cooling of transition metal dichalcogenide monolayers

Lasing cooling of semiconductors has been achieved by Zhang *et al.* for the first time in CdS nanobelts.²⁴⁸ The cooling mechanism is through the phonon-assisted upconversion photoluminescence, where more phonons are annihilated than created during the photo absorption and emission processes. Strong electron-phonon coupling and high photoluminescence quantum efficiency are two key factors to achieve net cooling in semiconductors. The former is required for the efficient annihilation of phonons (heat absorption) and the latter ensures little heat generation.

As direct semiconductors, the transition metal dichalcogenide monolayers exhibit strong upconversion photoluminescence when excited by photons with energy close but smaller than those of their optical gaps, which is a good sign of potential laser cooling. The upconversion PL spectra of 1TL WSe₂ excited by a 785 nm laser at different temperatures are shown in Figure 7-3a. The decreased PL intensity with decreasing temperature implies the phonon-assisted mechanism of the upconversion, since the phonon population is smaller at a lower temperature. Moreover, the integrated upconversion PL shows a linear relationship (see Figure 7-3b) with the excitation power in our experimental power range, ruling out the possibility of upconversion through two-photon or multi-phonon absorption, which further supports the proposed phonon-assisted mechanism.

Figure 7-3 Upconversion photoluminescence in 1TL WSe₂. (a) Temperature-dependent photoluminescence spectra excited by 785 nm laser. (b) Integrated PL intensity *versus* excitation power at 255 K. The red solid spheres are experimental data and the blue solid line is the linear fitting.

The phonon-assisted upconversion phenomena show promise for potential laser cooling in the transition metal dichalcogenide monolayers. The experimental demonstration requires the optimal sample treatment, as well as appropriate pump lasers and temperature sensing techniques, which will be systematically investigated in future research. Furthermore, it is essentially important to understand the detailed mechanism of the electron-phonon coupling in this family of materials, such as what type of phonons are involved into the upconversion process. A good knowledge of the electron phonon

interaction dynamics will show important guidance for the engineering their coupling strength and improve the heat absorption during the upconversion process.

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